

## ***Interactive comment on “Chemical mass balance of refractory particles ( $T = 300\text{ C}$ ) at the tropospheric research site Melpitz, Germany” by L. Poulain et al.***

**Anonymous Referee #2**

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The paper of Poulain et al. attempts a chemical mass balance of ambient particles by utilising a thermodenuder and various measurements to make a mass closure with the aim of characterising volatile (or refractory) fraction of ambient organic matter. The paper presents an ambitious attempt, but I am not sure if authors have realised all the ambiguities and uncertainties to make their work useful and inspiring for other researchers. The paper needs to be re-evaluated after major revision before considering it acceptable for publication.

The major problem starts with the title. Not only it brings uncertainty to the term “refractory”, but more importantly, how relevant is the use of thermodenuder in gaining insights

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about refractory nature of ambient organic matter. Refractory term should normally be used in circumstances when there is no ambiguity in the thermal decomposition. For example, AMS refractory mass is defined as flash evaporation of particles at 600C: temperature is arbitrary, but at least flash evaporation is instantaneous. The denuder based study is arbitrary both in temperature and the process of thermal breakup. To me the title should rather be about thermal stability or volatility of ambient particles and not the refractory nature at arbitrary chosen temperature.

Authors seem to suggest that  $T=300\text{C}$  is some sort of magic number everyone should follow. If not then how the results would compare if somebody runs the denuder at 250C, or a twice longer denuder. There is no information about the stability of the result if residence time was e.g. 10 times longer. For example, HTDMA community are in constant discussion and intercomparison of particle equilibration time in a humidifier (3, 6, 9 or even 30s) while the denuder with 1s residence time is assumed to be sufficient for thermally decomposing internally mixed aerosol. There is clearly a need running three denuders in sequence to see if volatile fraction changes as a result – otherwise what the current study tells us?

The other major problem is the implication that thermal decomposition is comparable to a fraction of LV-OOA derived by PMF. Authors rightly suggest that ammonium nitrate and ammonium sulphate decompose at temperatures below 200C, but is this true for highly internally mixed particles? If sulphate is (partially) coated by BC or humic like OM, will it decompose equally well within 1s residence time? If not then ROA is overestimated. If, similarly, there is significant amount of dust or processed dust ( $\text{CaSO}_4$ ) then ROA is also overestimated. More importantly, how the limited (ambiguous) particle volatility in the denuder is comparable to the fraction of non-volatile LV-OOA in terms of the chemical make-up? Taken the above altogether, I am not sure the term refractory is correctly used in the study and is useful to the community.

The uncertainties of the many parameters used in this study make the chemical balance very fragile. Authors may be right and lucky at the same when deriving rather

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arbitrary parameter like density. Will the same approach work in other geographical location? Given different density of OM, BC or the presence of crustal material, or significant amount of sea salt, may completely render the usefulness of the method. Or the PMF results at different location may suggest different partitioning between SV-OOA and LV-OOA which would suddenly result in different quantitative conclusions about volatile LV-OOA fraction. The results of this study are already suggesting about 50% uncertainty in refractory LV-OOA which is huge.

Some minor (other) comments

Abstract. Authors claim that their results suggest that organics was more volatile in summer, but the percentage of ROA was higher in summer (53%) then winter (47%). Something does not make sense.

P26987, line 16. Authors assert that AMS cannot detect sea salt, but that has been disproved by Ovadnevaite et al. 2012 (JGR). That study does not invalidate refractory nature of sea salt, but sea salt can certainly be quantitatively detected by AMS.

P26988. Authors rightly consider uncertainty in mass absorption coefficient, but that would introduce not only systematic uncertainty, but also would add significant variability as the mass absorption coefficient can be constantly changing. For example, absorbing humic like substances would result in higher mass absorption coefficient.

P26991, line 5. Authors assert TDMPs uncertainty at 10% (probably based on sizing precision in Wiedensohler et al (2012, AMT)), but it should rather be 33% due to volume conversion when making its use in mass balance.

P26992, line 9. R2 value is called "measure of determination", in other places "correlation", but in fact it is VARIANCE, or the percentage of the total variance explained by the common factor. The true correlation is "r", not R2.

P26992, line 19. Authors need a proof that ammonium sulphate evaporates at 150C in internally mixed particles, not only of pure species in laboratory setting. Please refer to

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consequences above.

Line 26. This is rather a major comment. Authors invoke the presence of marine particles when explaining strange mode at 400nm, but they quantitatively show that marine species contribution was small in PM2.5 and negligible in PM1. Something does not add up here. Can it be that larger particle could not reach thermal equilibrium in the denuder due to short residence time? Clearly, larger particles would require longer time to decompose inside out than smaller ones. This re-iterates the impact of residence time on the results. Was the size effect studied in at least laboratory setting?

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 26981, 2013.

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