**Anonymous Referee #1**

Received and published: 9 December 2013

*We would like to thank the referee for the constructive comments and suggestions made to improve the manuscript. Our responses are given below.*

The manuscript describes a reconstruction of chemical composition of refractory material (RM). RM is defined as the mass remaining in aerosol after passing a thermodenuder (TD) heated to 300_C. The reconstruction is achieved by comparing RM mass estimated using two methods. The first method combines black carbon and TD-DMPS measurements and uses an assumed particle density to arrive refractory mass concentration (RMC). The second method combines black carbon (BC) measurements with an estimate of refractory organic material, which is derived from LVOA factor in AMS measurements assuming that a fixed fraction of LVOA is refractory. The authors argue that RM measured with the TD system is composed practically completely of BC and refractory organics.

There are several major issues that need to be addressed before this manuscript can be accepted for publication.

The purpose of the presented work and its general usefulness is unclear. The definition of RM is strictly method-specific. A different TD temperature or a longer residence time will produce a different amount of material that remains in particles after passing the TD. Thus, the results presented in this paper are limited only to TD systems that are operated at the same temperature and residence time.

*Response: We fully understand the point of view of the referee. However, what he/she criticize in terms of "strictly method-specific" it is a common issue for any thermodenuder measurement, i.e. not exclusively specific to our work. Every TD measurement needs to opt for a specific temperature, residence time etc and the justifications for these parameters might differ from case to case. For this reason the working temperature was explicitly mentioned in the title of the manuscript as a reference value in order to provide an explicit definition of the term "non-volatility" used later on in the manuscript. We also noticeably mentioned intercomparison issues of TD measurements in the ACPD manuscript page 26994 line 10-14 ("[…] Although direct comparisons between the different TD measurement can be strongly influenced by the residence time of the particle inside the heated section (An et al., 2007), the previous works are in good agreement and confirm that a large fraction of the HULIS are not evaporated even after being heated at high temperatures […]").*

*Furthermore, we have to apologize for a mistake regarding residence times reporting in the manuscript. Based on the heated part of the thermodenuder (500 mm length and 20 mm internal diameter), the real residence times were 3.8 to 3.1 seconds for a flow rate of 2.5 and 3 l/min respectively. It will be corrected.*

*To provide a solid answer to whether the residence time in the thermodenuder might be appropriate for our purposes, we conducted a new experiment using our thermodenuder in question in February and March 2014. (This was, by the way, also requested by the second referee.) In this experiment, two technically identical mobility particle size spectrometers were set up at the research station Leipzig-TROPOS (Germany, urban background), each equipped with a technically identical thermodenuder upstream of the size spectrometer. The* *temperature in both thermodenuders was set to 300°C, as during the long-term measurements in Melpitz. The flow rate passing through one thermodenuder was kept constant, at 3.0 l/min while it ranged between 1 and 10 l/min in the second thermodenuder. Results of this sensitivity test reveal that no remarkable effect of thermodenuder flow rate could be seen on the remaining aerosol volume concentration, at least for our range of flow rate settings (1-10 l/min). We therefore see no indication that the residence time in the thermodenuder (3.1 s at Q = 3 l/min) would be insufficient to evaporate all particulate volatile material at 300°C. The results of this sensitivity test are relevant enough to be included as an Appendix in the manuscript and can be found in detail in our answer to the second referee.*

*As mentioned in the introduction of the manuscript, several studies emphasized that even after heating at high temperatures; a remaining organic fraction was measured (e.g. Wu et al., 2009; Huffman et al., 2009; Huffman et al., 2008; Faulhaber et al., 2009). This clearly indicates that a certain part of the particulate organic matter is made of non-volatile compounds. Although, only few direct measurements of non-volatile chemical composition have been made up to now, there are already a lot of thermodenuder measurements following change on aerosol number size distribution. For example, long term measurements made at the research station of Melpitz (continuously since 2002) as well as at six stations of the German Ultrafine Aerosol Network (GUAN, Birmili et al., 2009) since 2008 use the same type of thermodenuder working at a constant temperature of 300°C. Therefore, and as mentioned in the conclusion, our results might be extremely helpful to better understand and analyze such a dataset.*

*The following sentence will be added in the conclusion: "Nevertheless, our results clearly indicate that 300°C non-volatile organic matter might represent an important part of the non-volatile fraction of the atmospheric particles investigated in this work. Considering the limitation of our approach (i.e. proper mass balance closure of the ambient $PM_1$ and a minor contribution of dust and sea-salt to the total $PM_1$ mass), our findings could be used to extrapolate the maximum expected non-volatile organic mass concentration from similar setup measurements such as for the long term measurements at Melpitz and within the GUAN network".*

*Finally, our work also emphasized a large source of uncertainties resulting from the diameter shrink of super-µm particles to sub-µm size range that can strongly contribute to the overestimation of the non-volatile mass fraction of the particles. The influence of this artefact and the possible solutions to resolve it are also discussed and included in the section 3.4.1 and the conclusion of our manuscript ("[…] These results highlight the potential cross-sensitivity of partially volatile coarse mode particles on sub-µm volatility measurements, as long as these particles are not removed from the sample, e.g., by a pre-impactor. It might be desirable in the future to extend the V-TDMPS with an aerodynamic particles sizer (APS), or alternatively remove particles by a pre-impactor .")*

The purpose of reconstructing composition of RM, though not explicitly stated, appears to be to derive the amount of LVOA from measurements of RM with a TD system if BC concentration is known. For example, if 1 ug/m3 of RM is measured with a TD and there is 0.3 µg/m3 of BC, then, according to the authors, there should be 0.7 µg/m3 of refractory organics. If one uses a mass fraction remaining (MFR) for LVOA of 50%, the LVOA concentration can be estimated to be 1.4 µg/m3. This could be useful if one does not have an AMS available. However, as the authors point out in the manuscript, the

MFR of LVOA could vary by more than a factor of 1.5 (30% vs. 52%). Thus, such an estimate of LVOA is bound to be highly uncertain, especially if one takes into account uncertainties in measurements of BC, particle density, etc., in addition to the uncertainty in MFR.

*Response: The referee suggested an interesting approach. However, it was absolutely not considered in our manuscript. As mentioned by the referee, such indirect estimation of the ambient LV-OOA concentration would strongly depend on the value of the LV-OOA mass fraction remaining. Moreover, LV-OOA concentration estimated following this approach cannot be used to estimate either total organic mass or help to identify source composition of the rest of the organic.*

If I have misunderstood the authors and the purpose is the opposite, i.e., to derive the amount of RM from the AMS measurements, then it is not clear how useful this information is. The authors seem to equate the observed MFR at 300_C with aerosol volatility (see, for example, the abstract where the authors state that the aerosol was more volatile in summer than in winter). The TD temperature used in this study, however, is more suitable to characterize aerosol stability, not volatility. As the authors correctly point out, many inorganic molecules decompose at temperatures lower than 200_C. The same is true for organic compounds. The TD temperature used in this study is sufficient to break most common organic bonds, see figure 3 in Epstein et al. (Environ. Sci. Technol. 2010, 44, 743–748). Organic RM measured in this study most probably consists of decomposition products of high molecular weight compounds (many of which are admittedly LVOA). The amount of these decomposition products does not say much about aerosol volatility or the amount of low volatility compounds.

*Response: This is an important semantic point. Thermodenuder and V-TDMPS or V-SMPS are usually used to assess the aerosol volatility (e.g. Huffman et al., 2008; Wu et al., 2009; Wehner et al., 2002; Wehner et al., 2004; Philippin et al., 2004).*

*In previous work, Wu et al. (2009) compared the mass spectrum of humic and fulvic acids considered as surrogate for LV-OOA at ambient and 300°C. Although some modifications of the mass spectra were stated and attributed to the loss of water molecules and a small decarboxylation, the structure of the mass spectra was preserved and could still be compared to the ambient one. This was confirmed by Huffman et al. (2009) who successfully compared PMF results from ambient and coupled ambient-TD measurements and concluded that "any degradation of the mass spectra as a result of passage through the TD is compensated by the enhanced contrast between the different factors". Therefore, it appears to be accurate to use the ambient LVOOA mass concentration derived by PMF to estimate the non-volatile fraction when its remaining mass fraction at a defined temperature is known.*

*The text of the section 3.2.3 will be changed as follow: „Previous field measurements, using coupled TD-AMS set-up (Huffman et al., 2009) demonstrated that similar factor analysis components and time series results were observed when comparing ambient only PMF results with joint ambient-TD results. Therefore, it seems to be possible to extrapolate the non-volatile fraction at a specific temperature from the ambient PMF factors when their MFR at this temperature are known. […]. Additionally, changes of the mass spectra of the fulvic and humic acids at 300°C compared to the ambient mass spectra were attributed to the loss of water molecule and decarboxylation."*

The argument that RM is composed of only BC and refractory organics appears to be based on a comparison of two estimates, of which one uses a rather arbitrary assumption that the density of RM is 1.6 g/cm3, while the other depends on the assumed fraction of RM produced by LVOA. The density of graphitic material is 2.2-2.3 g/cm3; that of crustal material is similar. Thus, it is not clear why the value of 1.6 g/cm3 was chosen. If this value was chosen due to the presence of organic material in RM, it must then depend on the mass fraction of organics. This fraction varies not only with location but also with time due to varying contributions of different aerosol sources. As the authors show, even at one measurement location the refractory fraction of LVOA is not constant and can change by a factor of 1.5. The mass closure thus becomes subject to an arbitrary choice of parameters. Even if the conclusions presented by the authors are correct, their general applicability is questionable.

*Response: The referee mentioned here several of points that will be answered separately.*
*- Firstly, as already mentioned, only a small contribution of crustal material and sea-salt (both non-detected by AMS) might be expected on the* $PM_1$ *size range based on mass balance estimation (see Fig. 1 on the manuscript) and filter measurements. As mentioned in section 3.4.1, sea-salt contribution was only observed on some specific days of the winter period in the super µm fraction that was not considered in our study (out of the scan range of the TDMPS).*

*-We agree that particle density depends on the aerosol chemical composition as it was done for ambient measurements. However, since no direct measurement of the non-volatile chemical composition was made, it was not possible to use a similar approach for thermodenuder measurements. For this reason a constant value was used. The uncertainty due to the fixed density used on the estimation of the V-TDMPS non-volatile mass concentration was already included in the manuscript (p27000 l. 1: "Another source of uncertainty is the appropriate estimation of the refractory aerosol density. A constant value of 1.6 g* $cm^{-3}$ *was used, thus, changes of the density value will influence the present results.").*
*The sentence will be changed to better considered time and chemical dependency.*
*"Another source of uncertainty is the appropriate estimation of the non-volatile aerosol density which depends on the chemical composition of the non-volatile aerosol as previously seen for ambient measurements. Here a constant density value of 1.6 g* $cm^3$ *was used, thus, changes of the density value will influence the present results. Due to the uncertainty of the BC density and the real chemical composition of the non-volatile aerosol, an uncertainty of 10% can be reasonably expected. Considering the 10% of the V-TDMPS, a global uncertainty of 20% for the V-TDMPS mass concentration is estimated."*

*-It is absolutely true that providing an estimation of the BC density is quite difficult. As mentioned on the manuscript, a BC density of 1.77 g* $cm^{-3}$ *was considered to determine the ambient particle density in order to convert TDMPS volume concentration into mass concentration (Equation 1, from Salcedo et al., 2006). Density of BC is not so well defined in the literature compared to the density of, for example, ammonium sulfate or ammonium nitrate. The density of the BC depends on the type of BC and the form of the particles (aggregate, linear structure, shape…). The reported density values in the literature range from more than 2 g* $cm^{-3}$ *for pure graphite (Gysel et al., 2011) to lower values of 1 g* $cm^{-3}$ *(Hitzenberger et al., 1999). Moreover, recent studies reported values corresponding mainly to the value used in our manuscript. For example, Kondo et al. (2011) reported a density of 1.72 g* $cm^{-3}$ *for fullerene soot, and a density of 1.85 g* $cm^{-3}$ *was measured for the amorphous graphite (Kiselev et al., 2010). Park et al. (2004) demonstrated that after removing the volatile fraction, diesel soot particles have a density of 1.77 g* $cm^{-3}$ *independent of the particle*

*size in opposition to fresh diesel exhaust particles which have a size dependent density varying from 1.27 to 1.78 g cm$^{-3}$ in a size range of 50 to 220 nm (mobility diameter). Based on these different values, a density of 1.77 g cm$^{-3}$ for BC seems to be a relevant value for ambient BC to us. The previous discussion will be added in the supplementary information.*

*- We do not agree with the referee in that the change on the estimation of the LV-OOA mass fraction remaining reflects an uncertainty of 50%. Although similar PMF factor can be identified for 2 different measurement periods at the same location, it does not imply that the mass spectra of these two factors are ever 100% identical. Some variations on the mass spectra can result to changes of the initial sources (e.g. different biomass burning conditions) and/or different aging processes. Since the AMS and PMF cannot really describe the chemical composition of the organic aerosols, the better way to highlight these variations is to follow their oxidation level. Ng et al. (2010) summarized the changes in the oxidation level of different PMF factors obtained during several field campaigns over the northern hemisphere in a triangle space. The less oxygenated compounds are falling in the bottom of the triangle while during aging processes the OA tend to reach the top of the triangle space. Comparing factor analysis results of 25 AMS measurements across Europe,* Crippa et al. *(2014) provided an excellent demonstration of the diversity of the LV-OOA factor (Fig. SI-4 in Crippa et al., 2014). These differences between similarly identified factors might also lead to changes in the physical properties of the factors like hygroscopicity and volatility (Jimenez et al., 2009). Consequently, to better answer this question, the two LV-OOA mass spectra were compared in the Ng's triangle space. Results show that during winter, the LV-OOA was slightly more oxygenated than during summer which is in agreement with the idea that volatility of organic aerosol decrease with increase in the oxidation level (Jimenez et al., 2009). Consequently, changes of the volatility properties of the LV-OOA have to be considered as principally resulting from the differences in chemical composition (illustrated by the oxidation level of the factor) rather than related to solely uncertainties on the determination of the LV-OOA volatility.*

*The manuscript will be changed as follow:*

*"Differences in the volatility properties of the two LV-OOA factors may result from the difference in their oxidation states. To check this hypothesis, mass spectra differences were highlighted and plotted in Figure 7, f44 (the fraction of m/z44 to total organic mass spectra) vs. f43 (the fraction of m/z 43 to total organic mass spectra) in the triangular space presented by Ng et al. (2010). This triangle plot represents a simple and practical approach to compare different organic factors with different oxidation levels since they will fall in different area of the triangle. The less oxidized factors (e.g. HOA) are usually present in the bottom of the triangle whereas the most oxidized factors (e.g. LV-OOA) are usually present in the upper part of the triangle. The top part of the triangle tend to suggest that SOA oxidation level become more and more similar after long aging processes (Ng et al., 2010). Comparing the position of each LV-OOA factor highlights that winter LV-OOA was located slightly above the summer LV-OOA indicating that winter LV-OAA was more oxygenated than the one in summer. This small difference in term of oxidation state might explain the observed change in*

*the volatility properties of the two LV-OOA factors and the fact that the less volatile factor (winter time, MFR 52%) is also the one with the highest oxidation level."*

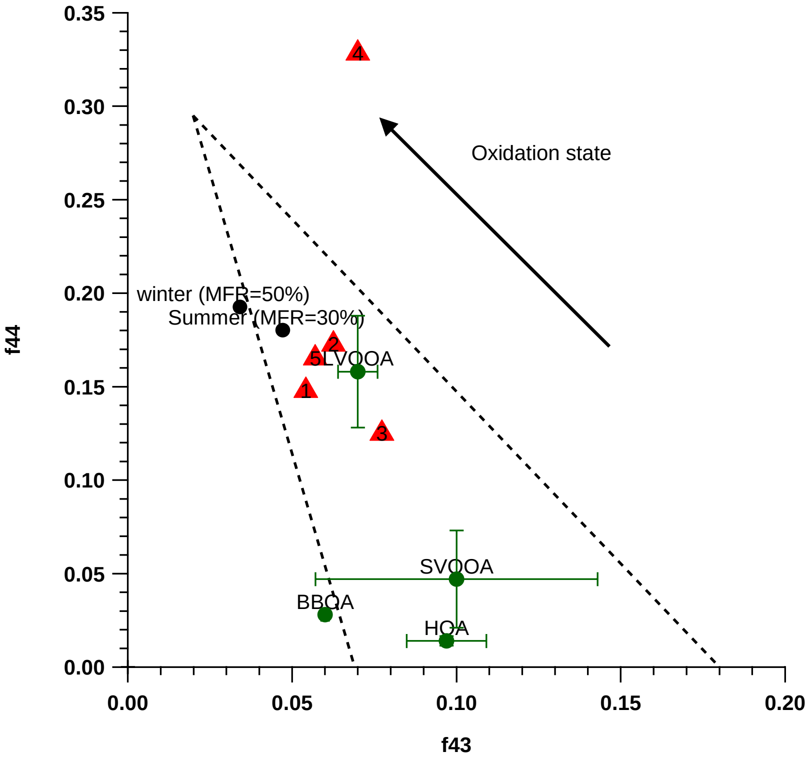

*Figure 7: f44 vs. f43 of each LV-OOA factors in the triangle space determined by Ng et al. (2010). The green points referred to the average values (+/- standard deviation) of factors used by Ng et al. (2010). Red triangle and numbers referred to different examples of LV-OOA factors (1: Hersey et al., 2011, 2: Lanz et al., 2007, 3: Ulbrich et al., 2009, 4: Robinson et al., 2011, 5: Crippa et al., 2013) illustrating the individual variability of LV-OOA.*

*Additionally, the sentence in the abstract was modified to: "Our results suggest that LV-OOA was more volatile in summer (May-June 2008) than in winter (February/March 2009) which was linked to a difference in oxidation levels (lower in summer)."*

The authors argue that a good correlation between the two estimates indicates that their hypothesis is correct, i.e., that the refractory material consists of BC and refractory organics. However, there could be other components in RM that correlate tightly with either BC or refractory organics. If this is the case (and the authors do not provide any proof that it is improbable), a good correlation between the two estimates would be preserved, but RM would contain other material in addition to BC and organics.

*Response: We agree with this point. However, possible contribution of unconsidered non-volatile material was mentioned and discussed in the ACPD manuscript for example at the end of section 3.2.2 ("It can be thought that other inorganic compounds, such as chloride, sodium, calcium, potassium, or magnesium remain in the particulate phase at 300°C") as well as later on section 3.4.2. ("Therefore, the presence of non-detected compounds like crustal material and/or sea-salts has to be considered. As previously mentioned, the contribution of non-measured inorganic ions represents 13% of the total* $PM_{2.5}$ *mass concentration in May/June 2008 and 4% of the total* $PM_1$ *mass concentration in February/March 2009. Additionally, identified species of daily* $PM_1$ *filter explain on average 80 ± 12% of the total filter mass in February/March 2009. Consequently, it is reasonable to consider that chemical particle composition was usually fully explained and that, finally, the non-considered compounds might have a small influence on the reconstruction of the refractory fraction within the uncertainties of the measurements. However, as mentioned earlier for the ambient mass closure, uncertainties on the MAAP and AMS measurements have also to be considered here)."*

*Therefore, our non-volatile OA mass concentrations corresponds more to the maximum refractory organics mass concentration that might be expected. It will be mentioned in the conclusion as follow: "Since contribution of undetected and non-volatile compounds (e.g. dust, other inorganic ions) cannot be completely excluded, the present non-volatile OA values have to be considered as the upper limit that might be expected for each period."*

The authors contradict their hypothesis when they discuss marine-influenced air masses. If there was indeed a significant contribution of marine aerosol to the fine fraction, then there should also be a significant contribution of sodium chloride and/or sodium sulfate. The argument that sodium hydrate is volatile is not tenable, because the only part that volatilizes is water, while sodium sulfate remains in the particles (its melting and boiling points are above 1000_C). Sodium sulfate comprises about 44% of sodium decahydrate mass. Thus, if there was a significant contribution of marine air, there should be a significant contribution of sodium salts to RM. The argument that there was a significant processing of marine aerosol and (probably) a large contribution of highly oxygenated organics is also tenuous – why would this secondary organics differ from other aged air masses that are not marine-influenced?

*Response: There seems to be a misunderstanding here on different particles size ranges (*$PM_1$ *and* $PM_{2.5}$*). As mentioned in the manuscript during winter campaign, chloride, sodium, calcium, potassium and magnesium all together represent around 4% of the total* $PM_1$ *mass. Consequently for the winter period, no significant marine particles can be expected in the submicron size range (*$PM_1$*). The marine aerosols mentioned in the manuscript and by the referee are located in the range 1-2.5µm, as demonstrated by impactor measurements presented in supplementary information which is outside of the scanning range of the V-TDMPS (< 800 nm). The discussion on the influence of marine air mass to the volatility measurements was made in order to explain the observed increase of the volume concentration for non-volatile particles mostly larger than 400 nm. The presence of these non-volatile particles was related to periods with the highest super-µm concentrations that typically happened under marine air masses influence during the winter time. These particles represent an important source of artefact for our volatility measurements since 1- there is no size cutting before the TD and consequently the entire* $PM_{10}$ *size range particles were introduced inside the TD and 2- the volume/mass fraction remaining is calculated as the ratio* *between volatility-TDMPS to ambient-TDMPS measurements with for each case has an upper size cutting of 800 nm. Consequently, when ambient particle larger than 800 nm (i.e. typically in our example marine particles) shrink to below 800 nm after passage through the TD, they will be counted by the V-TDMPS measurements and NOT by the ambient TDMPS leading to a strong overestimation of the volume fraction remaining as show in Fig. 2. In order to better consider this artefact for future volatility measurements; recommendations were explicitly made to the community for future V-TDMPS measurements.*

*- We thank the referee for her/his comment regarding the sodium sulfate volatility, this will be corrected.*

*- No on-line measurements of neither the volatility nor the absolute organic chemical composition of the super-µm particles was made and the discussion on the organic acids (p26997 l. 13 and following) was only made based on available literature to illustrate which compounds could be expected from the non-volatile super-µm aged marine particles. Several studies demonstrated that in the presence of sea-salt, organic acids could be present as sodium salts. Our laboratory measurements of succinic acids and disodium succinic acid highlight a huge difference in term of volatility between these two forms of succinic acid (the first one is semi-volatile and fully evaporated at 65°C while the second one present a MFR of 40% after passing the thermodenuder at 300°C) (Wu et al., 2009). This point appears to be important to emphasize since it can provide some idea on the non-volatile organic fraction of the super-µm particles and also suggests that volatility of organic compounds might be strongly influence by the sea-salt content of the particles. However, we are convinced that this is only some possible explanation and suggestion, and that more studies on the link between aerosol volatility and chemical composition in marine areas are needed.*

*The sentence was modified as follow: "Although a strong influence of the super-µm particles on the V-TDMPS measurements was clearly identify, it is not possible to provide a clear picture of the chemical composition of this non-volatile fraction, and to confirm or reject the presence of sodium salts in the resulting super-µm non-volatile fraction. This is because; no direct measurements of either super-µm particles or the aerosol chemical composition downstream of the TD were performed. The previous discussion based on laboratory volatility measurements and literature values indicates that the volatility of the marine particles can largely differ from those of continental origin."*

The calculated MFR is, as the authors admit, overestimated if the same upper size integration limit (800 nm) is used to calculate integrated volume of both original and thermodenuded aerosol. The authors thus propose to use a rather arbitrary boundary of 400 nm. A better method of correcting for the contribution of large particles is to calculate a new upper boundary for TD aerosol as dup =MFR1/3 800, then integrate TD size distribution to dup, calculate new MFR, and repeat these steps until changes in MFR become negligible with each additional iteration step (Stanier et al., 2004, Aerosol Sci. Technol., 38, 215–228). The authors should recalculate all the MFR data using that method and reanalyze the data.

*Response: We thank the referee for the interesting suggestion. The upper size cutting of 400 nm for the volatility measurements was not arbitrary selected. As mention in section 3.4.1 and in Figures 6 and 7, during both measurements periods, mean ambient particle size distribution showed a maximum below 400 nm. After passage through the thermodenuder,* *these particles will shrink to smaller size range. However, mean thermodenuder size distribution present a systematic increase of the aerosol concentration for particles larger than 400 nm. Since this size range (400 – 800 nm) was not present in ambient measurements, such an effect might result from either a diameter shrink of particles with diameter larger than 800 nm after passing the thermodenuder, or the presence of externally mixed particles made of pure non-volatile material.*

*Since super-µm particles were not measured in the ambient mode by the TDMPS (upper size range of 800 nm) counting of such particles by the V-TDMPS will lead to an overestimation of the non-volatile fraction.*

*As proposed by the referee, we investigated the upper size range of the volatility measurements based on the equation 2 of Stanier et al. (2004). A mean upper size range of 385+/- 40 nm and 441 +/- 77 nm was found for the summer and winter campaigns, respectively, which were in agreement with our estimation. The non-volatile volume concentration was recalculated for every sampling point according to the corresponding upper size range and our results were corrected according to the new estimation of the non-volatile fraction. The resulting non-volatile volume concentrations differ in average by less than 1% for the summer period and by 8% for the winter one.*

*The following description of this new approach will be included in the manuscript: "Since this artefact is strongly depending on the ambient super-µm particles concentration, a time dependent estimation of this contribution has to be made. Therefore, estimation of the upper size range of the TD measurements was made derived from the approach proposed by Stanier et al. (2004) for hygroscopicity measurements (equation 2).*

$$d_{max} = d_{800} \times \sqrt[3]{VFR_{800}} \qquad (2)$$

*where, $d_{max}$ represents the upper size range considered for the V-TDMPS measurements; $d_{800}$= 800 nm the upper size range of the ambient TDMPS and $VFR_{800}$ is the volume fraction remaining calculated using the entire V-TDMPS size range previously described. The time series of the $d_{max}$ value of each campaign is included in Figure 6. A mean upper size range of 385+/- 40 nm and 441 +/- 77 nm was found for the summer and winter campaigns respectively, in agreement with our estimation of an upper size cutting of 400 nm. According to that, the NVMC was recalculated using the obtained time dependent upper size range (Figures 3 to 6). "*

<u>Minor comments and corrections:</u>

p.26986, l.25: change "transmission" to "transport"

*Response: We disagree with the referee comment here. The official denomination of EMEP is "Co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe" as can be seen on the official website of the programme (www.emep.int)* p.26992, l.2: remove “as”

*Response: removed*

p.26996, l.9-12: One cannot make such a conclusion using the presented data. As Figure 7 shows, dV/dLogD of RM at any size larger than about 200 nm (and probably at smaller sizes too) is smaller than that of the original aerosol. If the aerosol is externally mixed with respect to RM, the measured RM size distribution would remain the same after the TD, but the volatile material would evaporate. The authors do not have enough evidence to prove otherwise.

*Response: The referee is right in commenting that we lack some essential information, notably on particle external mixture. We agree that the increase in non-volatile volume size distribution above 400 nm in Fig. 7 could, in principle, be explained by two rather different mechanisms: 1) say, there is a drastic change in external particle mixture at around 400 nm, with particles between 400 and 800 nm (and maybe even further above that diameter) containing a significantly higher fraction of entirely non-volatile particles. This would explain such an increase in non-volatile volume with increasing size. One could imagine such an effect to be caused by the presence of refractory dust particles, for example, in the sample aerosol. Option 2) would be the hypothesis that we outlined the shrinking of partially volatile particles with initial diameters bigger than 800 nm into the size range measurable by the V-TDMPS instrument.*

*For us, the reason to believe in hypothesis 2) is the conspicuous coincidence of the rather few episodes when the effect was observable, with the clear presence of maritime air masses that carried a measurable excess in chemical compounds pointing towards coarse particle sea spray as measured by Berner impactor measurements presented in supplementary information. Based on the existing long-term experience with chemical composition measurements at Melpitz, it appears extremely unlikely to us that it would be exactly those maritime air masses that would contain drastically enhanced fractions of entirely non-volatile particles, such as mineral dust or carbonaceous in sub-µm particles. (Indeed, the experience of long-term measurements at Melpitz tells that maritime airs contain rather low fractions of dust or carbonaceous particles).*

*With hindsight, our conclusion was probably formulated with too little reflection in the text.*

*We will therefore better explain our hypothesis in the revised version of the text, meanwhile pointing out that there is a certain deal of speculation involved. We believe that this effect, which we identified in the data is of strong relevance for the interpretation of long-term time series of the non-volatile particle volume, and thus prefer to keep the corresponding discussion within the revised manuscript.*

*The text will be modified to:”The non-volatile particles bigger than 400 nm might results either to a drastic change in external particle mixture with particles between 400 and 800 nm containing a significantly higher fraction of entirely non-volatile particles or to the shrinking of partially volatile particles with initial diameters bigger than 800 nm into the size range measurable by the V-TDMPS instrument. Presence of such particle was related to few episodes identify as corresponding to marine air masses (figure SI-3). Comparing the 5-stages Berner impactor samples performed for these specific days to the ones obtained during other air masses influence (Figure SI-4), emphasize the presence of a large coarse mode fraction during marine air masses (Figure SI-4). It is therefore our conclusion that the high value of measured NVMC can be influenced by marine super-µm particles which shrink* *during passage through the TD and move into the sub-µm measurement range of the TDMPS. However, in absence of direct measurement of the mixing state of the particle, we cannot completely exclude a minor influence of the mixing state of the particles. In some sense, this is a measurement artifact because these particles can only be detected by the TDMPS downstream of the thermodenuder, not upstream."*

p.26996, l.13: remove "principally"

*Response: removed*

p.26997, l.4: replace "more under continental" with "under stronger continental"

*Response: replaced*

p.26998, l.2-3: I do not think that a change in VFR from 11

*Response: It seems that a part of the comment is missing. However, we supposed that this comment was related to the change on the upper size cutting of the TD measurement to the mean VFR. In order to improve this point, the sentence will be revised as follow:*
*"The corrected results reveal that in average the VFR is still under the uncertainties of values obtained using the entire V-TDMPS size range* ($VFR_{(dmax)}$ *= 8±2% and 12±7% for 2008 and 2009, respectively).This indicates that during some specific periods, the upper size range of the V-TDMPS plays an important role in the estimation of the VFR. This is confirming our hypothesis that during such period, the presence of an artefact coming from shrinking of the super-µm particles to sub-µm size range when crossing the TD must be considered."*

p.26998, l.9: replace "in averaged for" with "on average"

*Response: replaced*

p.26998, l.23-24: Here the authors say that 13% and 4% refer to "the total mass", while the same numbers were attributed to "the total inorganic mass" on p.26993, l.1. Which one is correct? It should be also noted that the total mass of crustal material is larger than the mass of ions due to the presence of oxygen in oxides of metals and carbonates. Since the authors refer to ions, I assume filters were analyzed using ion chromatography. If this is the case, water-insoluble compounds would not be detected during the analysis.

*Response: We thank the referee to point out this error. We effectively referred to the total inorganic mass and not the total mass. Moreover, the unconsidered ions (chloride, sodium, calcium, potassium and magnesium) represent on average during the sampling periods 2.5% of the measured* $PM_1$*mass for winter time and 1.8% of the measured* $PM_{2.5}$ *mass for the summer time which are confirming their low contribution to the mass balance of the non-*

*volatile* $PM_1$*.Consequently, sentence on p26998, l.23-24 will be changed to "The contribution of non-considered water soluble inorganic ions (e.g. other water soluble ions like* $Ca^{2+}$, $Na^+$, $Mg^{2+}$ *and* $K^+$*) represents on averaged, 1.8% of the measured* $PM_{2.5}$ *mass concentration in May/June 2008 and 2.5% of the measured* $PM_1$ *mass in February/March 2009".*

*The sentence p26993 l.1 will also be changed to "Specifically, chloride, sodium, calcium, potassium and magnesium accounted for around 8% of the total identified inorganic* $PM_{2.5}$ *concentration and for around 4% of the identified inorganic* $PM_1$ *mass".*

*It is also true that all of our off-line ions measurements referred only to the water soluble ions and consequently non-water soluble ions are part of the non-explained fraction of the filter. It will be explicitly mentioned in the description of the off-line measurements as follow "Filters were weighted for the total particle mass and water soluble inorganic cations and anions as well as OC and EC were determined. Details on the different analytical methods and results for these two specific periods can be found in Spindler et al. (2010). Water insoluble ions, dust and metals were not measured and consequently contribute to the non-explained mass fraction of filters. On averaged, a mass recovery of around 82% was obtained for the* $PM_1$ *filters during winter time and 62% for the* $PM_{2.5}$ *filters during summer time. The lower recoveries value of the* $PM_{2.5}$ *filters compared to the* $PM_1$ *might be attributed to a larger contribution of crustal materials in the* $PM_{2.5}$ *size range compared to the one in* $PM_1$*"*

p.26998, l.15: replace "in opposite" with "in contrast"

*Response: replaced*

p.26999, l.19: "change of"

*Response: corrected*

p.26999, l.23: "upper size cut"

*Response: corrected*

p.26999, l.25: replace "is depending" with "depends"

*Response: replaced*

p.27000, l.3: remove "consequently,"

*Response: removed*

p.27000, l.13: replace “supplied” with “supplemented”

*Response: replaced*

p.27000, l.14: replace “might be” with “are”

*Response: replaced*

p.27001, l.6: replace “on oxidation states” with “of oxidation state”

*Response: corrected*

p.27001, l.9: replace “on” with “of”

*Response: replaced*

p.27001, l.14: Remove the last sentence because there is nothing in the manuscript that supports it.

*Response: removed*

Figure 5 caption: “the measured RMC” is confusing because it is not directly measured, it is estimated using an assumed density. I suggest using RMCBC,AMS and RMCDMPS instead of “RMCest” and “RMCmeas” throughout, because both parameters are partly based on measurements and estimates. The estimate based on the DMPS should not be referred to as “measured” in other parts of the manuscript either.

*Response: The nomenclature was changed to* $NVMC_{chem}$ *and* $NVMC_{V\text{-}TDMPS}$ *instead of* $RMC_{est}$ *and* $RMC_{meas}$.

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