We thank the reviewers for their comments. Our specific response can be found below. The reviewers' comments are in italics and changes made to the manuscript are in quotation marks. All the changes made do not affect the conclusions in the manuscript.

Response to Reviewer 1

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.

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* $\mu m^3/cm^3$*,* 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:* $\frac{dC_a}{dt} \approx \frac{\overline{C^*}}{\tau}$ *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.

Response: We appreciate reviewer's insightful suggestions/comments. The reviewer's key points and our responses/changes are listed below.

(1) Relationship between mass fraction remaining (MFR) and volatility. We acknowledge that MFR is not equivalent to volatility. Thus, we have added the following discussions in the revised manuscript.

"The thermal denuder (TD) has been used widely to measure the aerosol volatility (An et al., 2007; Huffman et al., 2008; Saleh et al., 2011a). Many previous studies inferred the volatility from the mass fraction remaining (MFR) or volume fraction remaining (VFR), which is calculated as the ratio of the species mass (or volume) concentration after heating to an elevated temperature in the TD to the species mass (or volume) concentration without heating (An et al., 2007; Huffman et al., 2009b; Jonsson et al., 2007; Lee et al., 2011; Stanier et al., 2007; Grieshop et al., 2009b; Xu et al., 2014; Huffman et al., 2009a). Larger MFR is used as an indication for lower volatility of aerosol. However, Saleh et al. (2011b) suggested that it can be misleading to use MFR as an indication of volatility. This is mainly because the MFR is an extensive parameter (which explicitly depends on the initial mass concentration) while aerosol volatility is an intensive property (which depends only on chemical nature of the compounds in a mixture). Instead of MFR, Saleh et al. (2011b) presented that the change in mass concentration when reaching equilibrium upon heating (i.e., ΔC) is an appropriate measure of volatility."

(2) Equilibrium timescale. With the reviewer's suggestion, we calculate the characteristic time for aerosol equilibration in the TD by following the algorithm in Saleh et al. (2011). The characteristic time is about 1600s, which is orders of magnitude longer than that residence time (i.e., 5s) in the TD. Since the evaporation process is likely far away from equilibrium, we adopt the reviewer's suggestion to use the change in concentration after heating in the TD (ΔC) to estimate volatility. We have modified the text in the revised manuscript.

"In this study, we calculate the characteristic time for aerosol equilibration by following the algorithm in Saleh et al. (2011b). To evaluate the equilibration time scale in the TD, the authors started with the mass transfer equation (Eq. (1)) and then obtained the characteristic time for aerosol equilibration (τ in Eq. (2)) by performing dimensional analysis.

$$\frac{dC_a}{dt} = -2\pi d_p D F N_{tot}(K C_{g,sat} - C_g) \qquad \text{Eq. (1)}$$

$$\tau = \frac{1}{2\pi d_p D F N_{tot}} \qquad \text{Eq. (2)}$$

$$F = \frac{1+Kn}{1+0.3773Kn+1.33Kn(1+Kn)/\partial} \qquad \text{Eq. (3)}$$

In the equations, C_a, C_g, and $C_{g,sat}$ are the aerosol phase concentration, gas phase concentration, and gas phase saturation concentration, respectively. N_{tot} is the total number concentration, d_p is the particle size, D is the diffusion coefficient in the gas phase, K is the Kelvin effect correction, and F is the Fuchs-Sutugin correction, which is calculated by Eq. (3). In Eq. (3), Kn is the Knudsen number and α is the accommodation coefficient. D is on the order of 10^{-5} m^2 s^{-1} according to Tang et al. (2015) and α is on the order of 0.1 as shown in Saleh et al. (2011a). By using the campaign-average particle number concentration (i.e., 4.28×10^3 cm^{-3}) and the mode of the particle number distribution (i.e., 87nm) in our study, we estimate that the characteristic equilibration time is about 1600s, which is orders of magnitude longer than that residence time (5s) in the TD. Since the evaporation process is likely far away from equilibrium, the gas phase saturation ratio is small and the particles are likely evaporating in a vapor-free environment. Under this assumption, the gas phase vapor concentration (i.e., C_g) in the mass transfer equation (Eq. (1)) can be neglected. After integration over the residence time in the TD, the change in mass concentration upon heating (ΔC_a) can be calculated by Eq. (4), in which $t_{residence}$ is the residence time in TD and the $\overline{C^*}$ is the evaporation-time-averaged saturation concentration. Thus, the ΔC_a for each component is proportional to its $\overline{C^*}$ because the other parameters are the same assuming the compounds are internally mixed.

$$\Delta C_a = C_{t=0} - C_{t_{residence}} = \int_0^{t_{residence}} \frac{KC_{g,sat}}{\tau} dt = \frac{t_{residence}}{\tau} K\overline{C^*} \qquad \text{Eq. (4)”}$$

By using this method, we find that the ΔC’s of three OA factors are not statistically different at 120°C. This suggests that although the O:C of OOA (O:C = 0.92) is substantially larger than that of HOA (O:C = 0.22) and SFOA (O:C = 0.37), the volatilities of the three factors are similar at 120°C. This is consistent with our conclusion that the average O:C may not be a good indicator of OA volatility. We have modified the manuscript accordingly.

(3) Statement that OOA is the main contributor to the extremely low volatility compounds. In the original manuscript, we only state that OOA is the main contributor to the residual OA at 250°C, instead of main contributor to the extremely low volatility compounds. For example, in the

conclusion part of our original manuscript, we stated that "We note that 16% of total OA remains even after heating at 250°C, suggesting the existence of non-volatile organics. PMF analysis reveals that the majority of the remaining organics are oxygenated OA." Our statement is based on fig. 10, which clearly shows that the mass fraction of OOA in total PM_1 at 250°C is substantially larger than that of HOA and SFOA.

(4) Explanation for the "strange" relationship between MFR and O:C. While we cannot rule out the possibility that the difference in OA concentration between studies contribute to the various relationships between MFR and O:C, the distribution of O:C and volatility likely plays a more important role. For example, in Donahue et al. (2012), the O:C increases while the MFR decreases during the photochemical aging of α-pinene ozonolysis SOA. This anti-correlation between O:C and MFR cannot be explained by the dependence of MFR on OA concentration. This is because the OA concentration increases and the MFR decreases during the aging, which causes the ΔC to increase. The increase in both O:C and ΔC still indicates that the OA becomes more volatile as it is more oxidized.

We acknowledge that there are other possible explanations for the various relationship between O:C and MFR and we have added the following sentence.

"In addition to the distribution of O:C and volatility, the fact that MFR depends on the initial concentration of OA, which is different between studies, may also contribute to the various relationships between O:C and MFR."

Other comments:

1. p. 23181, 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.

Response: For the urban site, only the HR-ToF-AMS measurements are used in this study. We have added the following discussions in the revised manuscript.

"For instruments deployed at the urban NK site, only the high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne) ambient measurements are included in this study. The data analysis of HR-ToF-AMS at the urban site is similar to that at the rural site, which will be discussed below. Details regarding the measurements at the NK site can be found in *Young et al. (2015a)*."

2. 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).

Response: We have modified the text and added Saleh et al., 2011 as a reference. The sentence now reads as the following.

"The time scale to reach thermodynamic equilibrium in a given TD depends on a number of factors, such as TD temperature, aerosol mass concentration, aerosol diameter, and mass accommodation coefficient (*An et al., 2007; Riipinen et al., 2010; Saleh et al., 2011)*."

3. 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 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.

Response: We have modified the discussion as shown above (i.e., the response to your major comment).

4. 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.

Response: Firstly, we thank the reviewer for this suggestion. However, we feel like that it is useful to include the discussion regarding the particle density in the main text. Importantly, the discussion highlights the uncertainties in AMS collection efficiency in TD measurements.

Secondly, we have checked the SMPS volume distribution under different TD temperatures. As shown in the figure R1, the mode in the volume distribution is 345, 290, and 290 nm for bypass line, TD 120°C, and TD 250°C, respectively. The volume distribution under three temperatures largely overlap the region where the AMS lens transmission efficiency is close to unity (Liu et al., 2007). Thus, the shift in size distribution does not affect the intercomparison.

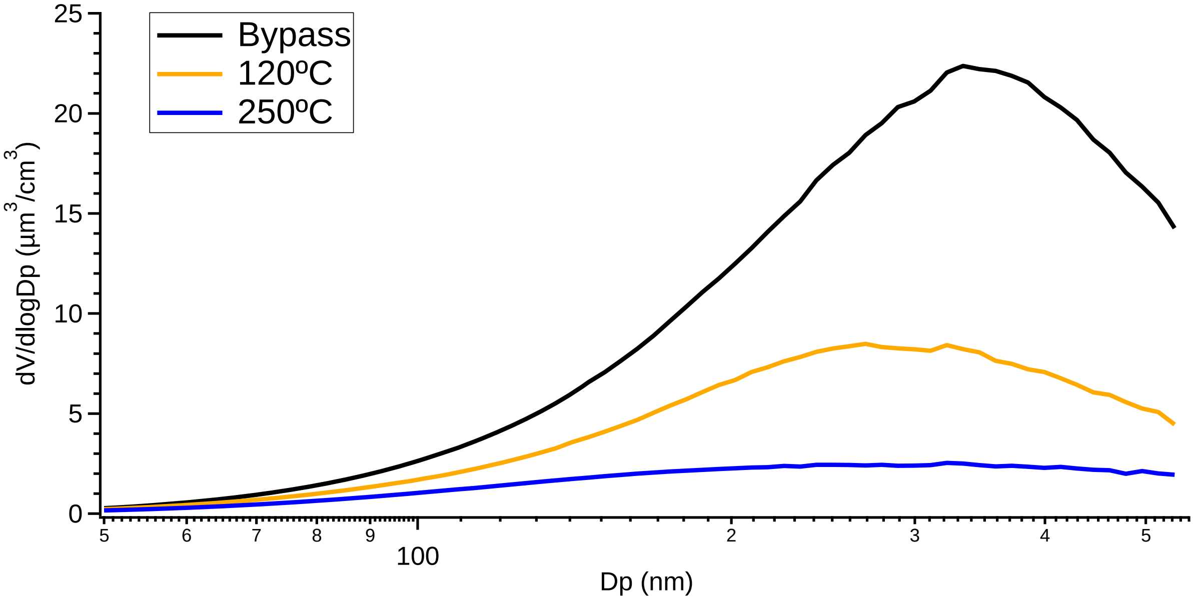

Figure R1. Campaign-average volume size distribution for bypass line, TD 120°C, and TD 250°C.

Thirdly, we also thank the reviewer's suggestion regarding calculating the black carbon density based on the comparison between SP2 and SP-AMS. However, there are some uncertainties associated with this method, such as the shape factor of black carbon and the size distribution measured by SP2, which is beyond the scope of this manuscript. The BC particles get coated quickly in the atmosphere, therefore we use the bulk density for the bypass line. However, the BC coating is mostly removed in the TD after heating so that we use the effective density for the TD line.

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

Response: The NO^+/NO_2^+ ratio of organic nitrate ranges from 5 to 10, which is about 2 – 4 times larger than that of ammonium nitrate. The 10-20% of the difference shown in Fig. S12 is likely within the uncertainty of the NO^+/NO_2^+ ratio of ammonium nitrate, which has been discussed in detail in a recent publication by Xu et al. (2015).

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

Response: Figure 3 (line 3) is introduced before figure 4 (line 18).

7. 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.

Response: Since submitting the manuscript, we continued to investigate the reason for the higher sulfate and OOA concentration at the rural Detling site. Based on the results from an atmospheric chemistry transport model (Ots et al., 2015), we find that the higher concentration at the rural site is a result of meteorological conditions, which cause a strong gradient of SOA concentration when air masses are advected from polluted mainland Europe.

Ots et al. (2015) applied the regional EMEP4UK (European Monitoring and Evaluation Programme) model, which uses 5 km by 5 km British Isles grid nested within 50 km by 50 km greater Europe domain, 21 vertical levels, Weather Research and Forecasting (WRF) model meteorological reanalysis, and National Atmospheric Emissions Inventory (NAEI) for the UK, Centre on Emission Inventories and Projections (CEIP) emissions for other European countries. The figure below shows the daily-averaged modelled SOA concentrations from Feb 4 to Feb 7. The white circles mark the urban NK site (left) and rural Detling site (right). They observed a steep negative gradient of SOA concentration from near European continent to southern England. The steep gradient is a result of meteorological conditions (i.e., mainly wind direction), which causes that the pollution plume from mainland Europe largely passes over the rural site, but not the urban site. This is consistent with our measurements. Detailed descriptions about the model and comparison between model and measurements can be found in Ots et al. (2015).

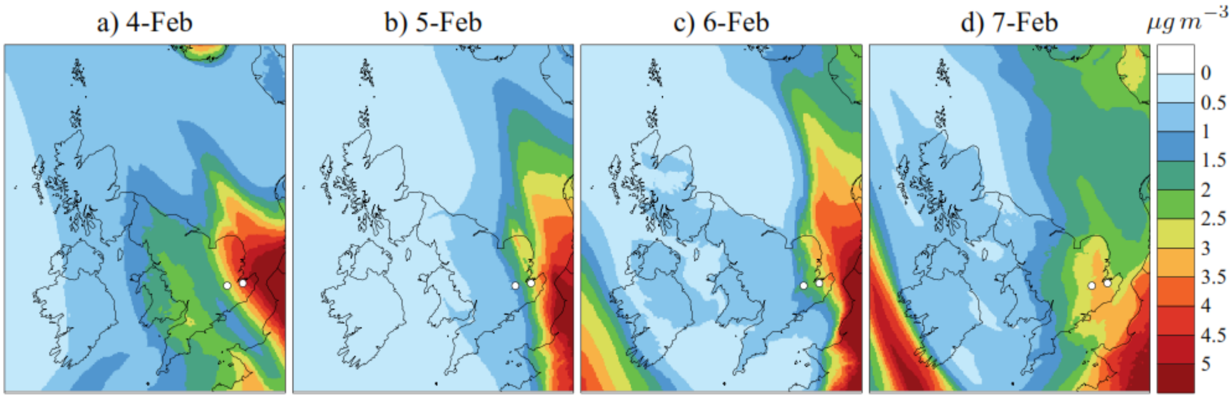

Figure R2. Modelled daily-average SOA concentration from Feb 4 to Feb 7, 2012. The white circles mark the urban NK site (left) and the rural Detling site (right). Adapted from Ots et al. (2015).

We have modified the text accordingly in the revised manuscript to discuss the results from Ots et al. (2015) and offer an explanation for higher sulfate and OOA concentration at the rural Detling site.

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

Response: We thank the reviewer for the suggestion. We have modified the text accordingly throughout the manuscript.

9. 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.

Response: In the manuscript, we did not discuss the volatility of rBC coating. In figure 11, we compared the residual coating on rBC with residual bulk OA after heating to 250°C to provide insights about the sources of non-volatile organics.

10. 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.

Response: We propose that the distribution of O:C is one possible explanation for the various relationships between MFR and average O:C of bulk OA. The explanation proposed by the reviewer has been incorporated in the revised manuscript. We refer the reviewer to the response to your major comment.

Response to Reviewer 2

1. Although the authors performed retroplume analysis, inclusion of wind direction would be helpful, at least a wind rose plot showing the prevailing wind during this study.

Response: We have added the wind rose plot in the revised supplemental information (Figure S1(b)).

2. The average wind speed was 5.8 m s $^{-1}$*, and the distance between the two site is 45 km. This means that the transport time from the urban site to the rural site was generally within 2 hours. Could the authors explain how biomass burning aerosol can be rapidly oxidized to OOA in such a short time in winter when photochemical processing is often weak?*

Response: In this study, most of the air masses are easterly (i.e., mainland Europe), so we did not sample the urban outflow from London. Based on the results from an atmospheric chemistry transport model (Ots et al., 2015), the higher OOA concentration at the rural site is a result of meteorological conditions, which cause a strong gradient of SOA concentration when air masses are advected from polluted mainland Europe. We refer the reviewer to the response to comment #7 of reviewer #1.

3. Page 23816, line 10, no Eq. (4).

Response: Thanks for the note. We have deleted “Eq. (4)” in the sentence.

4. The OA fraction of the campaign average at the Detling site was the same in Figure 3 and Figure 6. Could it be some mistake since the organics loading and the period for the calculation was different.

Response: This is just a coincidence. The mass fractions are different if using three significant digits. For example, the mass fraction of HOA at the Detling site is 19.3% in figure 3 (average of the whole campaign period) and 18.6% in figure 6 (average for periods when instruments at both sites were operative).

5. I am thinking if it is appropriate to connect the three points using straight lines in Figure 9 since the relationship is not linear.

Response: The points are connected by lines to guide the eyes. We have added this in the figure caption.

6. Change “(b)” to “(b – e)” in the caption of Figure 12.

Response: We have modified the caption accordingly.

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