

Responses to reviewer #3

The authors appreciate the helpful comments by the reviewer #3 for improving the manuscript. Below is the point by point response for the detail comments.

Reviewer comment # 1

“Why did the authors chose to conduct this study at a rural site in southern Ontario? This question is important and specifically pertains to the reliability of the PSAP (Particle Soot Absorption Photometer) measurements which are known to be highly uncertain. Secondly, filter based absorption measurements are riddled with problems (because of the fibrous nature of the filters). Particles can travel deep into the pore spaces, flatten out on the surface, coagulate, and/or absorb to the individual fibers of the filter substrate. An excellent review of the associated problems with filter-based absorption measurements for thermal analysis and PSAP was presented by Subramanian et al. 2007 published in Aerosol Science and Technology.”

The reviewer also makes the related comment in their overview paragraph: “It is important to note upfront, that the sample collection methods for the three analyses are very different and also that this study was conducted at a site with very low OC concentrations ranging from 1 to 2.5 $\mu\text{g}/\text{m}^3$.”

Response to comment #1

We assume that the comment about the choice of measurement site is because the reviewer believes these mass concentration levels are low. But the reviewer provides no guideline here as to what are the appropriate concentration levels to study. The reviewer suggests that our OC mass concentrations range from 1-2.5 $\mu\text{g m}^{-3}$, whereas the actual OC range is up to about 6 $\mu\text{g m}^{-3}$ (Figure 1). The OM mass concentrations are significantly higher. The site experiences a wide range of aerosol mass concentrations due to the impacts from various sources, which is one reason it was chosen. Another important reason for conducting such measurements at this site is that it is subject to a more processed aerosol (e.g. condensation of sulphate, nitrate, SOA) than is found in an urban environment. Such conditions make this site optimum for this type of study.

We agree that there are limitations to the use of the PSAP; at the time of the study these methods were all that were available to us. That said, we discussed in the original manuscript the uncertainties associated with using the PSAP for light absorption. We find no reason that these uncertainties will change our basic findings, and other than raising the issue (again) the reviewer has not demonstrated that either.

Reviewer comment #2

“Related to number 1, how do or will the authors address the differences between these two methods?”

Response to comment #2

We can only see reference to the PSAP in the reviewer’s first comment. It is unclear to us what other method we are supposed to compare to? Again, we discussed the PSAP limitations in the original manuscript.

It is assumed that the two methods mentioned by the reviewer are the PSAP and the thermal method used in the study. As Subramanian et al. (2007) pointed out that the laser based thermal optical analyzer (TOA) may have trouble to separate OC from EC properly in biomass burning samples due to the differences in attenuation coefficient

between the brown carbon/liquid OC and the EC originally collected on the filters, the authors would like to clarify that the method used for determining OC, POC and EC in this manuscript is not a laser-based thermal-optical method but a thermal evolution (including pyrolysis and combustion) method combined with a stable isotope approach (Huang, et al., 2006). The definition of POC is not the same as the POC in thermal-optical methods although they may be related to (also see the response to the reviewer#1). Thus, the absorption measurements by PSAP and the OC, POC, EC measurements by the thermal method, in nature, are two independent datasets.

Reviewer comment #3

The determination of POC has been well understood to be problematic. As the authors point out the temperature step between 570C and 800C includes charred organic carbon and carbonate carbon. Additionally the laser attenuation correction is difficult because the charred OC can be often darker than EC on the filter. It appears to me that the new thermal analysis method reported in Huang et al., 2006 varies substantially from other highly used thermal optical method protocols such as IMPROVE and NIOSH. Since so many conclusions in this paper hinge on the correctness of the determinations of OC, POC, and EC, it would have been nice to see some comparison of the results between the analytical methods. I assumed this was done in the previous studies, but did not find it in the cited literature.

Response to comment #3

As we know, the determinations of OC, POC and EC are dependent on the methods/protocols used and currently, there are no internationally accepted standards used for such measurements. In the widely used IMPROVE and NIOSH methods, the OC and EC split is determined based on the laser reflectance or transmittance with an assumption of the same attenuation coefficient (AC) between POC (i.e., the charred OC) and EC. However, as reported by Subramanian et al. 2007, the POC and EC often have different AC, thus, the thermal-optical methods may have problems to properly quantify the POC and to separate OC from EC. Whereas, in the method used in this study, the OC, POC, and EC are determined only based on thermal evolution, including pyrolysis and combustion at three temperature plateaus with optimized retention times. Stable carbon isotope is also used to distinguish POC from carbonate carbon (CC). The comparison between this method and IMPROVE and NIOSH has been provided in the response to the referee#1 (a slide presented in the black carbon section at EGU-2009).

Reviewer comment #4

It has not been proven by Huang et al., 2006 or others (to my knowledge) that the POC is directly proportional to oxygenated organic compounds. The referenced paper states, "Most of the pyrolyzed organic carbon (POC), (formed through charring during the thermal evolution process), possibly some remaining OC-based compounds (e.g. high molecular weight refractory carbon), and carbonate carbon (CC) are released at 870 C." Further the Huang et al. paper reports very limited data corresponding to the POC time segment; the only oxygenated compounds they studied were sucrose and glucose. The nature of the OC is very important. A number of studies have presented findings of oligomers formed by esterification reactions. What about nitrooxy sulfates, organic sulfates, organic nitrates? How do these compounds behave in the thermal analysis? Since standards are not available it's difficult to say at present. But it is important to note, that there are many hundreds of unidentified oxygenated organic compounds that may evolve between the OC and/or POC temperature steps.

Response to comment #4

As we know, understanding/quantifying POC is important to determine OC and EC and properly determinations of OC and EC are challenging in ambient aerosol studies.

As mentioned before, the POC defined in this thermal method is *different* from the POC determined by the widely used thermal-optical methods (e.g. IMPROVE and NIOSH). The POC from this method is the total carbon mass released between 550°C and 870°C under oxygen-free He flow (see page 14323, line14-19), which includes three components i.e., (1) carbonate carbon, (2) charred carbon at temperatures up to 550°C (likely due to the existing of oxygenated OC), and (3) the refractory OC (including both oxygenated and non-oxygenated) that possess relatively high bonding energy and could not be released completely at temperatures up to 550°C. Stable carbon isotope is used to further constrain the POC.

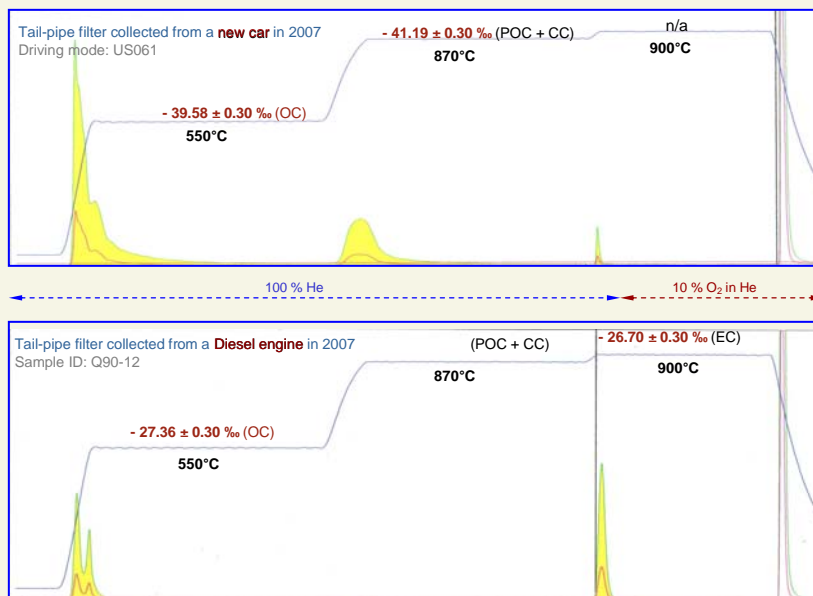
In 2006 paper, we applied this method not only to two oxygenated OC (i.e., sucrose and glucose) but also to more than 10 n-alkens and PAHs (see the Fig.6 and Fig7 of the 2006 paper). Although this method used for n-alkanes and PAHs included more temperature steps, it was shown that no POC fractions were identified in the pure n-alkanes and PAHs at 870°C temperature plateaus.

As the reviewer mentioned, yes, there are many hundreds of oxygenated OC exists in the ambient aerosols, including organic sulphates, organic nitrates, and lots of them could not be even identified. At 870°C, those organic compounds associated oxygen are likely decomposed into carbon monoxide as a result of high temperature vaporization detected by the thermal analysis. Further detailed laboratory studies for those compounds will be conducted in future but they are beyond the scope of this manuscript.

Yes, the nature of OC is important for the POC quantification (see attached an unpublished figure), the results from directly collections of tail-pipe emissions show that the filter from gasoline emissions contains much more POC than that from diesel emissions. Although we could only analyze the limited organic compounds as lab standards, this does not prevent us from verifying the finding (i.e., POC is related to oxygenated OC) by corresponding measurements in ambient environments as well as from specific emission sources. The linear relationship between POC and (OM-OC_{total}) in ambient aerosols at Egbert demonstrates that POC is proportional to the oxygen mass in PM

The text related POC in the revised version will be modified to clarify the puzzles the reviewers had and to avoid any potential confusion.

Carbon Isotope of OC/EC in PM from Transportation Emissions (VPDBCO₂ scale)



Reviewer comment #5

Given the high uncertainty of the AMS OM determination described by the authors in lines 378 through 391, the data collected by the alternate method cannot validate the OM/OC ratio determination directly from thermal analysis.

Response to comment #5

We agree with the reviewer that comparability of the OM/OC determined from this study with that from other studies available from the literature is uncertain, but that does not prevent comparison. Different methods are subject to different assumptions and uncertainties. We clearly identify the possible factors affecting comparisons with our results. We do suggest this is a validation.

Reviewer comment #6

The long discussion of the ambient measurements does not add to this paper. The ambient measurements were divided quite substantially into sources by wind direction. The primary wind direction has to be at least 40% of the time. This is very low. Also the division of the samples makes the sample sets for correlation analysis small. Further, the source attribution assignments need to be confirmed with molecular marker analysis or AMS data. I did not understand it there is more related data or not in another paper, but if so the results should be at least summarized here.

Response to comment #6

We apologize for not including wind data in the original manuscript, and we have added a table in the appendix of the revised manuscript to address this. In the analysis, the occurrence for the two wind sectors (north and south) was determined for all the filter sampling periods. Taking the wind speed into account, almost all the data defined as either north or south have more than a 80% contribution from the corresponding direction sector (except one with a 50%). In many cases, the wind occurrence is almost completely contributed from one direction sector.

The differentiation between the biogenic and anthropogenic emissions used in this manuscript is also supported by Slowik et al. (2009). For example, during the biogenic period impacted dominantly by the air masses from the north, acetylene (a long-lived anthropogenic tracer) mixing ratios remained very low while there was an increase in concentration of monoterpene. On the other hand, for the air masses from the south, a much sharply increased in acetylene concentration was observed. Furthermore, increased in concentration for aromatic VOCs, NO_x, and particulate sulfate were also observed. The authors have included these descriptions in the revised manuscript.

Slowik, J.G., Stroud, C., Bottenheim, J.W., Brickell, P.C., Chang, R.Y.W., Liggio, J., Makar, P.A., Martin, R.V., Moran, M.D., Shantz, N.C., Sjostedt, S.J., van Donkelaar, A., Vlasenko, A., Wiebe, H.A., Xia, A.G., Zhang, J., Leaitch, W.R., and Abbatt, J.P.D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, *Atmos. Chem. Phys. Discuss.*, 9, 18113-18158, 2009.

Reviewer comment #7

Related to the site location and aerosol aging, the authors need to recognize that EC also undergoes chemical transformation in the atmosphere and may diminish with time (Decesari et al., *Atmos. Env.* 2002).

Response to comment #7

The authors thank the reviewer for pointing out the Decesari et al paper. As mentioned in the paper, soot, a form of the material commonly referred to as black carbon, originates from combustion processes and is a mixture of elemental carbon (EC) and organic compounds (OC). Decesari et al reported that a group of water soluble organic carbon (WSOC) in aerosols, identified as humic-like substances (HULIS), can be produced by atmospheric oxidations of soot, inferring a chemical transformation from less hydrophilic OC to more hydrophilic OC.

We will refer to the possibility of such transformation contributing to our result.

Reviewer comment #8

There is a conceptual misunderstanding in the introduction. In lines 52-57, there is a description of the OC sources: primary emissions, "condensation of the low-volatility primary emitted organic gases, and secondary organic aerosol (SOA) formation via photochemical oxidation: : ." Gas to particle condensation of low volatility gases is not likely since dilution increases the volatilization of gases. This is governed by the partitioning equilibrium between a gas and a solid. Now on the other hand, partitioning from gas to liquid with aqueous transformation (aka aqueous SOA formation or cloud processing), may be possible. The aqueous phase pathways and other heterogeneous reactions alter the chemistry and particle morphology, thus potentially altering substantially the aerosol properties observed at a rural site. I recommend the authors review Poschl *Angewandte Chemie-Int. Ed.* 2005 to update the aerosol aging and transformation processes.

Response to comment #8

The authors thank the reviewer for pointing out the proper wording to use in the introduction. The corresponding revision has been made in the revised manuscript.

Reviewer comment #9

The abstract was poorly written. I would prefer to read first why the paper and findings report within are important, brief notes of the instrument method or unique analysis, and major conclusions and implications. There are a few sentences that read too much like other sentences in the text (methods and results) and a few that are

worded strangely and thus are confusing. The description of the air masses from the south: : : and those from the north: : : need revision/clarification.

Response to comment #9

The authors thank the reviewer for the suggestion. It has been revised in the revised manuscript.

Reviewer comment #10

A decreasing trend: : : sounds better than a decrease trend: : : see line 38.

Response to comment #10

This change has been made in the revised manuscript.

Reviewer comment #11

Biogenic influence versus SOA? Where do we draw the line? Obviously SOA can arise from either biogenic or anthropogenic emissions. As presented in a few papers, most notably Volkamer et al. GRL 2006 which was titled, "Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected," that SOA is quite substantial in anthropogenic emissions. Biogenic influenced SOA may look different, but the molecular properties are not well understood.

Response to comment #11

The biogenic period referred to here is based on many observations, including those from the AMS and PTRMS. The detail measurements and methodology are given by Slowik et al. (2009), which is available in ACPD. We have corrected the text to clarify that SOA arises from anthropogenic and biogenic precursors.

Reviewer comment #12

The authors indicate as a main objective to determine "the relationship between POC and the degree of oxygenation/aging." I don't see how this is possible. First, POC is not agreed upon nor proven. Second, the degree of oxygenation/aging cannot be estimated by thermal analysis, AMS OM determination, and/or PSAP. The chemistry is complex and cannot be presented without comparison to controlled studies.

Response to comment #12

The authors agree with the reviewer that the issue is complex (refer to the response to comment #4), but it should be still encouraged to understand/explore the issue via different approaches, e.g. Integrating different datasets in ambient aerosol measurements (including chemical and optical characteristics). Regardless of how complex the chemistry is, a relatively strong relationship between what is defined here as POC and the amount of oxygen mass ($OM-OC_{total}$) in the aerosol is found from the present results; the r^2 is 0.84 for 32 data points in Figure 6.

Reviewer comment #13

Related to #12, the third objective of the paper is to "examine the influence of POC and sulfate as the impact of aerosol aging on the SAC to estimate the value of SAC of primary emitted soot particles." Here the authors extend uncertain conclusions to PSAP data collected in a relatively clean site. The uncertainty of the instrument is too high for "clean" sites.

Response to comment #13

As discussed for comment #1, the site is not as clean as the reviewer suggests. We demonstrate a decreasing trend of the SAC with POC and with sulphate, including the uncertainties. There is nothing wrong with doing that. In the revised manuscript, we have improved our handling on uncertainty by replacing the figure of SAC vs. POC by SAC vs. particle mass loading ($OM + SO_4^{2-} + NO_3^-$). The point here is to show that SAC

decreases with increasing degree of aerosol secondary processing/photochemical-oxidation.

Reviewer comment #14

PSAP data must be corrected. The Bond et al., 1999 citation is a good start, but it's not the definitive answer to PSAP correction. Generally, parallel absorption measurements using a photoacoustic or nephelometer are collected for an accurate determination of the correction factors. Since the applied correction factors are a vital component in your data QA process, they need to be specifically described here and compared if possible to other correction methods to substantiate the paper conclusions.

Response to comment #14

The reviewer suggested correcting the PSAP data with scattering based on Bond et al. (1999). The presented measurement in the current manuscript is not corrected for scattering but corrected for flow and filter spot area. One reason the presented absorption data was not corrected for scattering is because part of the scattering data was not available during the field study.

Based on the original equation presented in Bond et al., it was stated that about 2% of the observed particle light absorption is a result of scattering and therefore required to be corrected. When applying the scattering correction to data whenever scattering data is available, there is a decrease in absorption measurement from 5 to 10%. This results an even larger slope in Figure 8 of the original manuscript. The original Bond correction for PSAP data is primarily for measurements taken from urban measurements where light scattering due to the presence of organic and inorganic coating seems to lead to light absorption enhancement. The authors are unsure if the same can be said for a rural site when some observations from literature show that decrease in light absorption could be possible due to processing (e.g., Liousse et al., 1993; Lewis et al., 2009). As a result, the correction is not done to the measurements.

Lewis, K. A., W. P. Arnott, H. Moosmüller, R. K. Chakrabarty, C. M. Carrico, S. M. Kreidenweis, D. E. Day, W. C. Malm, A. Laskin, J.-L. Jimenez, J. A. Huffman, I. M. Ulbrich, T. B. Onasch, A. Trimborn, L. Lui, and M. I. Mishchenko (2009). Reduction in Biomass Burning Aerosol Light Absorption upon Humidification: Roles of Inorganically-Induced Hygroscopicity, Particle Collapse, and Photoacoustic Heat and Mass Transfer. *Atm. Chem. Phys. Discuss.* 9, 15247-15294.

Reviewer comment #15

Related to sampling protocols and collection efficiencies, the authors compare 1-minute PSAP data to 24 hour integrated filter samples for thermal analysis? This sounds like another source of big error and uncertainty.

Response to comment #15

The PSAP data were averaged to cover the same sampling period as the integrated filter samples. This reduces the uncertainty in the PSAP measurement taking into account of that the filter transmission was always >0.5.

Reviewer comment #16

How was the biogenic period determined? The description in lines 274-276 is very short and refers to yet another outside paper. Related to the above comments, I recommend brief summary of key findings with the reference to substantiate these claims.

Response to comment #16

The biogenic period is determined by a number of factors including source region (based on trajectory analyses), observations of the aerosol composition (from the AMS) and gaseous precursors (from the PTR-MS). There are many details that are given by Slowik et al. (ACPD, 2009) and which are beyond the scope of this paper.

Reviewer comment #17

Line 288, "The difference in concentration: : ." What difference do the authors refer to?

Response to comment #17

In the previous sentence, we discuss the difference in concentrations of OC, POC, EC, OM, and Basp between the northern air masses and the southern air masses. The word "the difference" in the following sentence refers to the "south - north concentration difference". This difference in concentration is smaller when comparing the biogenic period with the southern air masses. This sentence is revised for clarification.

Reviewer comment #18

Paragraph in lines 306 to 324, summarizes the data tables without adding much to my understanding of why this data is important. I recommend that a few key findings be presented with supporting data and leave the mundane in the table without additional description.

Response to comment #18

Suggestion from the reviewer was taken and the corresponding section in the revised manuscript has been modified.

Reviewer comment #19

Correlations given in the paper tend to be fairly weak. Although, it seems likely that some relationships are identifiable, the cause of the relationships are not substantiated by the statistics.

Response to comment #19

We are unclear about the particular correlations that the reviewer is referring to as weak. Assuming the reviewer is referring to the relationship between SAC and POC (i.e., Figure 8). This regression suffers from the relatively low concentration of POC in general, and leads to concern from reviewer #2 that the uncertainties from the independent variable may be significant compared to that for the dependent variable that the uncertainties of dependent and independent variables would have to be considered. To overcome this problem, the authors have decided to replace this figure with the relationship between SAC and $(OM + SO_4^{2-} + NO_3^-)$. The rationale is that OM, SO_4^{2-} and NO_3^- are likely oxidation products. By using the sum of all three species would allow the authors to demonstrate the observation of the decrease in SAC for more processed aerosols. Also, this will reduce the relative uncertainties in the independent variable and makes the ordinary linear least squares more robust. Also, in the new figure, it is very clear despite of the decreasing trend in SAC, there is also a distinct difference between the north and south groups; this also illustrates that the method for wind origin separation used in this manuscript is reasonable.

Reviewer comment #20

Easy target: two AMS instruments don't agree well with each other? This is a red flag that the cross comparison of the various methodology don't necessarily agree well either. Collection efficiencies and sample collection intervals and times are very likely causes of the weak correlations. Also keeping in mind the rural site which is relatively

clean, thus the uncertainties are quite substantial compared to the measured/determined values.

Response to comment #20

There are differences between the two AMS used during the two studies. During 2005, a Q-AMS was used to measure the OM. During 2007, a higher resolution C-ToF AMS was used to measure the OM. Biases, if there are any, do not affect correlations. As we point out in our response to comment #1, the site is not as “clean” as the reviewer suggests.

Because of the much longer sampling times and considerably fewer data points, we have adopted the suggestions of this reviewer and reviewer #2 and removed the 2005 measurements from the revised manuscript. This does not affect the conclusions and substantially simplifies the paper.

Reviewer comment #21

What is TE?

Response to comment #21

TE refers to AMS transmission efficiency and it is defined in p.14324 line 22 in the original manuscript.

Reviewer comment #22

The ratio of toluene and benzene seems irrelevant with respect to the site's emission sources. The particle aging that may be determined from this ratio is only that originating from vehicular emissions. Thus, there is a relative particle aging for some of the aerosol, but aerosol is a complex mixture (internal or externally mixed) of particles from several sources (vehicle emissions, biomass combustion, cooking, biogenic SOA, aqueous SOA (aka cloud processing), anthropogenic SOA, etc.).

Response to comment #22

We agree with the reviewer. That is the reason that this ratio is not solely used as the "aerosol age indicator" in the manuscript. Also, the authors have revised the manuscript to avoid using the phrase “age indicator” to avoid confusion. The main point that the authors would like to bring out is the “degree of oxidation” or the “oxygen level” of the aerosol particle, which is not necessary always linearly proportional to the particle age. As demonstrated in the manuscript, the “oxidation level” in the aerosol particle is related to the POC defined in our thermal method and also appears to relate to the observed SAC change.

Reviewer comment #23

If the authors can substantiate the POC determination and the babs measurement from PSAP, then I would find the relationship between SAC and POC to be more interesting. At this point, I feel this is highly speculative. Also the plots shown in Figures 6, 7, and 8 are too scattered with too much information to be helpful. This section alone could be made into an excellent paper with more complete error analysis and after the ambient measurements are verified by at least the inclusion of the AMS data. Again a major stumbling block here is the validity of the PSAP data in a “clean” ambient environment.

Response to comment #23

The scatter in Figure 8 is partly due to the low concentration of POC, and so we have changed the independent variable to the sum of OM, SO_4^{2-} and NO_3^- . Despite this significant change, the tendency in the data points remains the same. This new figure shows that there is something fundamental about the soot structure over time that is not normally expected. This change in structure is not likely to affect the thermal

measurement but appears to affect the optical measurement. In the current manuscript the authors suggested the collapse of soot structure is one possible reason, and we have added possible chemical change as the reviewer suggests in their comment #7 above.

Terms such as black carbon and elemental carbon are often used in literature to refer to similar substances but they can be different as mentioned in Decesari et al paper. The light absorption coefficient obtained from PSAP reflects the amount of light absorbing carbon. The EC obtained from thermal method indicates the amount of carbonaceous material released at 900°C with the presence of 10% oxygen. Some scatter is expected because some EC may not be as light absorbing as other EC and because some light absorbing material may not be EC. Nevertheless, the coefficient of determination between EC and light absorption is strong (0.81). Given the solid physical basis for a connection between the two, Figure 7 provides validation of the PSAP. We have improved the clarity of Figures 7 and 8.

A main theme of the reviewer's criticism is that the site is clean. We have addressed that in response to comments above, and it would seem that the reviewer has overlooked the true range of concentrations. The site provides a good range of concentrations, and our observations produce a result that is contrary to that expected; the data do not indicate the expected rise in SAC with increased levels of materials that may coat EC. We can not offer any conclusive explanation(s), but the result is important.

Reviewer comment #24

Minor errors are found throughout the text. Some are simple grammar and some are typos. One important typo is the dates in Figure 1. Figures and tables don't show data. The authors present data in tables and figures. Line 493 found should be find. Line 337 is should be was. "Values in Table 2a represent: ::" in line 307 should be reworted. Line 166, last should be lasted. Just to name a few.

Response to comment #24

Typos are corrected in the revised manuscript, and the grammar has been improved.