

Interactive comment on “Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms” by S. Gilardoni et al.

Anonymous Referee #1

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1. Does the paper address relevant scientific questions within the scope of ACP? YES
2. Does the paper present novel concepts, ideas, tools, or data? YES 3. Are substantial conclusions reached? YES 4. Are the scientific methods and assumptions valid and clearly outlined? NO 5. Are the results sufficient to support the interpretations and conclusions? YES 6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? NO 7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? YES 8. Does the title clearly reflect the contents of the paper? YES 9. Does the abstract provide a concise and complete summary? YES 10. Is the overall presentation well structured and clear? NO 11. Is the language fluent and precise? YES 12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? YES 13. Should any parts of the paper (text, formu-

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lae, figures, tables) be clarified, reduced, combined, or eliminated? NO 14. Are the number and quality of references appropriate? YES 15. Is the amount and quality of supplementary material appropriate? YES

This manuscript describes functional group, OC and OM measurements taken on aerosol particles sampled during the MIRAGE 2006 campaign using FTIR and AMS. I believe that this manuscript is a valuable contribution to the MILAGRO special issue because it is probably the most comprehensive semi-quantitative analysis of organic functionality I have seen from MILAGRO. These measurements get to the heart of identifying the chemical nature of organic aerosol while avoiding instrumentally defined quantities. This paper has a wealth of information, but I believe it can be improved in several areas by adding some additional discussion points outlined in the “general comments” section below. The general comments also point out a few technical issues regarding data interpretation. The most important scientific question I would like to see the authors address is related to how the presence of organonitrates might affect their results.

The paper can be improved considerably by working on organization and flow. For instance, I thought the most insightful observations were buried at the end of the results section. To pull the reader in to the paper, they may want to put those results up front. The introduction section included some general information about primary and secondary organic aerosol, but did not adequately state what questions were to be answered here. I also found it difficult to decipher how the FTIR method was carried out even after reading the references that were included in the experimental section. Perhaps this is due to my lack of knowledge of the FTIR technique, but I think that the authors need to tailor their experimental section to scientists who are experts in atmospheric chemistry, but not necessarily experts at aerosol FTIR sample workup and analysis. Clarification of the methods sections is essential for a reader trying to understand the results. So, in conclusion, the results are interesting, but I think the paper needs more work before being published.

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General Comments

The authors mention OM/OC ratios several times in the abstract and at the end of the introduction without a proper introduction of what that quantity means or why it is useful to measure. OM and OC are mentioned separately in section 3.1, but again, the quantities are not really well defined at that point. A very technical definition is found in the methods section but is of little help to the reader. A nice general physical interpretation is given later in the paper (p 6632 line 15). Such an interpretation should be used to guide readers who are not familiar with this technical definition. I recommend including a few sentences discussing the utility of the OM/OC ratio in the introduction.

P 6620, line 10: Robinson et al. have shown that organics volatilized from POA may be an important source of SOA. This should be indicated at this point in the manuscript.

From reading the introduction, I do not really get a sense of why the authors are performing the measurements they have carried out. Why should OM/OC be measured? Why should functional groups be measured? What are the outstanding questions to be answered? This paper presents some nice results which are, with out a doubt, useful; the authors need to demonstrate this in the introduction. The sentence on line 6 of p 6621 is a step in this direction, but does not provide any references demonstrating why OA is so poorly characterized and what remains to be done.

Methods: The sampling is poorly described. Over what dates were samples collected? Were any sampling dates missed? What were the dates of the flights that the C130 data was extracted from? Were data used from all flights? This is especially important for readers trying to compare this paper with others found in the special issue.

The authors mention that the uncertainty of their method is between 5 and 21% and then give reference to several papers in which their method is developed. In 2/3 of those references, they state that their method provides an “estimation” of the functional group concentration. My question is: what does an uncertainty mean when it is applied to an “estimation”? Does this quoted range of uncertainty take into account the full

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range of possible systematic errors? If not, then what are the possible errors?

The authors mention the possibility for organosulfates to complicate the analysis, but I am curious to know how organonitrates would affect the data-especially in light of findings by Ziemann (oxidation of alkanes in the presence of NO_x), Seinfeld (oxidation of isoprene in presence of NO_x) and many others. How capable is the FTIR method at identifying organonitrates? Some discussion of this is needed because organonitrates could affect OM/OC ratios.

P 6624, Line 26: Is the correlation coefficient between the FTIR and the AMS really 0.69? The correlation looks much worse than the correlation at Altzomoni ($r^2=0.62$). Furthermore, there is no linear fit shown for the C130 data. If the authors are going to report a correlation coefficient, they should also show the fit on the figure. Furthermore, the legend of the figure reads as if the linear fit is shown on the figure. This needs to be fixed. Consistency between figures is needed.

P 6626, Line 9: The use of Aiken et al., 2008 is questionable because it presupposes that the AMS would detect organosulfates by a fragment containing C and S. Aiken et al. mention that organonitrates and organosulfates may pose a problem for OM/OC characterization by the AMS. If the organosulfates fragmented to give AMS sulfate, then one would also expect that sulfate calculated from the elemental sulfur concentration to match AMS sulfate; the authors mention here is indeed the case. However the authors here use this as argument against organosulfates, which is not necessarily correct given the reasons I have stated above. I think this paragraph should be revised to consider the limitations of the analytical methods- both AMS and FTIR. This discussion also applies to P. 6632, Line 25.

A few times (P. 6627, Line 27 & P. 6633, Line 3) in the manuscript the authors argue that the usual direction of transport is from the south to the north and then go on to reference various meteorological articles. As is evidenced by these meteorological studies, the airflow patterns in the Mexico City basin can be complicated depending on

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a number of different factors including time of day and synoptic conditions. I think the authors should compare their sample times with (readily available) back trajectories to bolster their claim that the data was usually capturing south to north transport. If those conditions were not always sampled, then what fraction of the samples had this sort of transport?

P 6628, Line 3: Besides just temperature and RH, I think it would also be useful to show total mass concentrations measured with some standard methods since the authors are discussing mass. This would allow the reader to evaluate whether just organics were enhanced during a particular period, or if the total mass was as well. Such a comparison would also allow the readers to see how much of the total mass was actually organic. These measurements should be readily available.

Page 6629, Line 9: The correlation between K and C-OH groups reported in Liu et al. was not particularly high ($r^2=0.61$) as might be expected given the variability of that ratio with source. The authors should quote the correlation obtained in Liu et al. and perhaps discuss why a high correlation should be expected or why it wasn't as robust as the correlation between, say, Si and Al.

Page 6630, Line 9: I think it might be useful for the authors discuss possible sources of heavy oil combustion besides just stating "industry". What about power plants? A quick web search tells us that "conventional thermal" energy is the primary energy source for Mexico (<http://www.eia.doe.gov/emeu/cabs/Mexico/Electricity.html>). This conventional thermal makes use of heavy fuel oil.

P. 6630, Line 21: Please use the correlation coefficient (instead of confidence intervals) here to be consistent with the rest of the paper. Also, scatterplots might demonstrate a good correlation rather than overlaying time series. The correlation does not look especially good. Furthermore, how do we know that the timeseries correlation isn't controlled by dilution? It would be interesting to correct for dilution and see if any correlation remains.

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Comment

P. 6632, Line 21: I consider a “rinse” and an “extraction” to be very similar. The authors state that the FTIR method does not involve solvent extraction. However, the references documenting the method used here indicate solvent rinses. If this is the case, this should be mentioned. If rinses were not used, then the method should be better documented in the methods section.

P. 6634, Line 20 & P. 6635, Line 2: the authors state the OM/OC ratio is higher at Altomomi (0.11) than it is at the urban site (0.10) and go on to discuss reasons why this may be. Given the scatter of the points in figure 9 and the stated error of up to 20%, is the difference in OM/OC ratio significant? Is a discussion over this small difference meaningful?

Fig 2: Why does the AMS data always fall at one extreme of the FTIR data in this figure? It is either at the highest or lowest end of the range reported by the FTIR. This is odd. Please either fix the problem or discuss why this behavior is seen.

Minor Corrections

P. 6620, Line 28: The sentence starting on this line is awkward; the authors should rewrite this.

P. 6621, Line 21: More precise coordinates should be given to the reader so they can pinpoint the exact site.

P. 6625, Line 19: The authors should state what platform this sentence refers to.

P. 6625, Line 25: It would be nice if the authors could indicate why the amine concentration is so uncertain. This should be stated here to allow for a full interpretation by the reader.

P. 6634, Line 6: The first sentence of this paragraph is long and confusing-clarification is needed.

Fig 2: Why are there errorbars on fig 2b and not 2a. Also a fit should be shown on fig

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2b.

Fig 2c: label the x axis

Fig 3: This is a nice way to parse the data. It would be nice to see if there are any trends with the aliphatics.

Figures in general: Many of the colors appear without legends. It would be quicker and easier for the reader to decipher what is going on without having to read the caption. Also, the yellow shows up as orange on my computer.

Fig 5. Would be nice to have a legend here.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 6617, 2009.

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