Atmos. Chem. Phys. Discuss., 9, C1716–C1725, 2009
www.atmos-chem-phys-discuss.net/9/C1716/2009/

Atmospheric Chemistry and Physics Discussions

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

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Received and published: 10 June 2009

The authors are very grateful to the reviewers for their constructive comments. We have revised the analysis of the data collected on board the C-130 with the use of Flexpart retroplume calculations and the data published by Tie et al 2009. The Flexpart revision of the C130 changed the upper bound of functional group composition, leading to a larger uncertainty in the contribution of carboxylic acids to organic mass and a smaller uncertainty in amine group fractions.

To pull the reader into the paper, as suggested by the first reviewer, the most insightful observations are mentioned at the end of the introduction section. The introduction itself is modified in order to better state the goal of the study. We have included additional details on the experimental methods by repeating information that was

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previously cited from other papers in order to make the FTIR analysis method more clear. Several of the figures have been modified to improve clarity, as suggested by the reviewers, and these figures are posted with the revised manuscript to avoid redundancy in this response.

Responses to Referee #1

General comments

1. We agree with the suggestion of the reviewer on the need of a better explanation on the utility and on the physical and chemical interpretation of the OM/OC ratio. The introduction is modified accordingly:

"The aerosol organic mass, here calculated as the sum of organic functional group masses, consists of carbon and hetero-atoms (i.e. oxygen, nitrogen, sulfur, hydrogen) that are bonded to the carbon skeleton of the organic compounds. The mass of organic aerosols composed mainly by aliphatic and aromatic hydrocarbons (like freshly emitted aerosols) is close to the sum of the carbon atom masses; the mass of organic aerosols characterized by oxidized molecules includes the contributions of oxygen, nitrogen, and sulfur atoms in addition to the carbon mass. The organic mass to organic carbon ratio (OM/OC) is an index of the contribution of hetero–atoms to the organic mass: chemically processed particles are expected to have higher OM/OC ratio compared to freshly emitted and unprocessed aerosols. The OM/OC ratio also relates to the contribution of organic carbon (measured with evolved gas) to the total particulate mass. As such, the OM/OC ratio together with the molar ratio of oxygenated functional groups relative to aliphatic C–H groups are used here as metrics of both increases in hetero–atoms and oxidation. which result from atmospheric processing (sometimes called aging) during the MIRAGE campaign at three sites."

2. P6620 line 10. In order to clarify the sources of SOA, the reference Robinson et al.

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2009 is added as suggested.

3. The purpose of the paper is reformulated and better stated in the introduction:

"The organic functional group composition provides information about aerosol sources, aerosol aging, and air mass processing. The results presented here show that the contribution of oxidized functional groups to OM is generally larger in the urban plume".

4. Sampling dates for the C130 are now specified in Fig. 1 and listed in the experimental section; we have also replaced flight numbers with dates on Fig. 4.

5. We agree that confusion might arise from the use of the terms "estimates" and "uncertainty" in previous papers. We have used the term "estimate" to remind the reader that the uncertainty in the approach is typically 20%, so as to minimize the potential for it to be interpreted in the same way as a "standard" quantitative measurement, which might typically have uncertainty of less than 5% for most reported values. We note that in doing so we are being more conservative than the community, and so we have removed this usage here. (As an example, AMS OM measurements are conservatively estimated to have an uncertainty of 30%, yet these measurements are typically not reported as "estimates" in the sense that we have intended here. Another example is WSOC, which have uncertainty associated with the solubility of the organics mixtures in which they are measured, easily making it more of an "estimate" than a reproducibly measured quantity for any specific organic compound.)

6. Organonitrates were investigated using two absorption signals at 1275 and 857 cm^{-1}. These signals were below detection limit at all three sites during the entire campaign. Based on the range of detection limits for the samples collected in this study, the upper bound on the contribution to OM of organonitrates is lower than 5%.

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The absence of organonitrates in clarified in the text.

7. The number of points for the AMS / FTIR comparison is too low to justify a linear fit. For this reason the line is omitted in Fig. 2b. This is already mentioned in the text and now clarified in the caption.

8. We agree with the reviewer that the AMS-XRF agreement is consistent with the absence of organosulfates but is not sufficient to establish that absence. Recent unpublished results by one of the authors (Jimenez) may lend additional strength to this argument, but are not available for citation in this work. The text has been modified accordingly. The following sentence is added to the text: “The nearly 1:1 ratio is consistent with the low concentrations of organosulfate reported by FTIR, although this observation is not sufficient for an independent confirmation."

9. We agree on the need of stronger evidence to point out the influence of urban plume. Flexpart retroplumes are used to support that data were capturing south to north transport. Flexpart results show that more than 70% of the C130 samples for which OM/OC data are available correspond to south-to-north transport conditions. This observation is mentioned in the text. In addition, we have refocused Fig. 8c to only show the south to north transport events that originate in the city.

10. Figure 4 is updated with aerosol mass data at SIMAT ($PM_{2.5}$ from beta measurements); no direct measurements of particle mass were available at Altzomoni. Text and caption are updated. While mass at SIMAT typically exceed OM (as expected), the high-OM events are typically not seen as high-PM.

11. The correlation coefficient of K and alcohol group (r^2 = 0.61) is not particularly

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high compared to correlation of soil elements. This is due to the variability of emission factor for biomass burning molecular markers, depending on combustion conditions, biomass type (i.e. grass or wood), and biomass composition (Fine et al. 2001, Jordan et al. 2005). This is specified in the text:

"The correlation coefficient of K and alcohol C-OH group (r^2 = 0.61) is lower than correlation of soil elements to each other. This lower correlation is expected because of the variability in the emission factors for biomass burning molecular markers, depending on combustion conditions, biomass type (i.e. grass or wood), and biomass composition".

12. Energy production is added as one of the potential sources of heavy oil combustion products at P6630 line 10.

13. P6630 line 22: the correlation coefficient of K and aliphatic saturated group is reported in the text. In addition concentrations of potassium and aliphatic saturated C-C-H are divided by carbon monoxide concentration (CO) to correct for dilution, and the good correlation is preserved.

14. Spectra acquisition method is clarified in the experimental section.

15. We acknowledge that the difference between SIMAT and Altzomoni ratio is small; we have removed the sentence at P6634 lines 20–22.

16. Figure 2d is revised.

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The sentence at P6620 line 28 is revised and the coordinates of SIMAT (19°24′12″N 99°10′34″W) are now specified with higher precision.

P6625 line 19: The sentence is modified to make clear that the sentence refers to the C130 dataset only rather than the project overall.

The large uncertainty observed on the C130 is due to variability of carboxylic acid group. The reason is now clarified in the text:

“The upper bound of functional group composition is calculated assuming that the concentration values below detection limit were equal to the detection limit itself. This assumption leads to large variability for the COOH group due to its high absorbtivity (Table 1)."

Sentence at P6634 line 6 is reformulated.

Error bars are omitted in Fig. 2a to avoid confusion, due to the larger number of data points compared to Fig. 2b. This is clarified in the figure caption.

X-axis in Fig. 2c is now labeled.

Figure 3d is updated with aliphatic saturated functional group and the figure comment is updated.

Legends added to Fig. 2, 3 and 5.

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Responses to Referee #2

General comments

1. We agree on the usefulness of plume evolution data reported by other authors to understand variability of OA composition. We merged information from C130 flight classification from Tie et al. 2009 and Flexpart retroplume analysis to select C130 filters that sampled the urban plume and compared their composition to C130 samples affected by background pollutants. The result of the comparison is shown in Fig. 3d. We have modified this to highlight the specific events that our discussion focused on. The following paragraph is added to the result section:

"Tie et al. use meteorological data and CO measurements to identify the periods when the C130 flights intercepted the urban plume and background air masses. Flexpart retroplume trajectories are used to identify urban plume and background samples among filters collected during research flight 2, 3, 6, 8, and 11. These flights were chosen because they included Mexico City overpasses, sampling of urban plume at different distance form the source, and collection of background samples. During flight 6 the aircraft intercepted the urban plume only during the last part of the flight, and during flight 11 the flight track was mostly located upwind of the plume. Samples collected during the first part of flight 6 and during flight 11 represent background aerosol. Samples collected during the central part of flight 2 and 8 and the last part of flight 3 are representative of the urban plume. Figure 3d compares functional group compositions of plume and background samples. On average background aerosol masses showed a slightly larger contribution of alcohol groups and a smaller contribution of aliphatic saturated groups; the differences are within the variability ranges because of the variability of aerosol composition with plume age."

2. The elemental analysis results at SIMAT have been better linked to previous works related to industrial emissions in the Tula area. Figure 5 is modified to make the time

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series readable.

3. We are grateful to the reviewer to point out the need of a more rigorous discussion about the oxidation of the aerosol masses sampled during the C130 flights. To investigate the variability of OM/OC ratio as a function of aerosol sources, and not just sampling position, Figure 8c is updated in order to display the results from plume and background sample analysis. The figure comment is added at P6634 line 4.

"The flight tracks that intercepted the urban plume are reported in Fig. 8c while those that sampled background air masses are reported in Fig. 8d. Background air masses exhibit OM/OC values larger than those measured close to the urban area but smaller than values observed for urban plume far north of the city. The increase of OM/OC for plume samples is likely due to different aging and processing of sampled air masses."

The contribution of COOH to OM observed by the C130 over the city is comparable to the contribution observed at SIMAT.

4. The sentence at P6634 lines 20-22 has been removed. Figure 9 is modified and COOH and C-C-H molar concentrations are normalized by carbon monoxide concentrations. A second panel is added to Fig. 9 and the ratio COOH to C-C-H is investigated as a function of particle age defined by the ratio OM to CO. The following paragraph is added to the result section:

"DeCarlo et al. (2008) compute the OM to CO ratio from aircraft measurements and relate it to the age of the particles; in fact OM is expected to increase with SOA formation, while carbon monoxide is a tracer for recent emissions, typically of combustion. The correlation between particle age and OM to CO ratio implies that OM and CO have a common source so that dilution is compensated by CO normalization. The OM to CO ratio on the C130 ranged between 70 and 90 μg m^{-3} ppm^{-1}. Figure 9b shows

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the COOH to C-C-H ratios at SIMAT and Altzomoni as a function of the OM to CO ratio. At SIMAT aged particles characterized by OM to CO larger than 20 μg m^{-3} ppm^{-1} had COOH to C-C-H ratio larger than 0.08, while smaller ratios were observed for less aged particles. Altzomoni had usually higher C=O to C-C-H ratios than SIMAT, likely due to aerosol processing or rural air masses. Figure 9b reports the linear fit function of SIMAT measurements and shows a weak correlation ($r = 0.38$) between COOH to C-C-H ratio and OM to CO ratio; considering the wide range of particle sources and their mixtures, this weak correlation explains a significant amount of the variability in the acid fraction. The fitting line has a positive slope consistent with the increase of COOH to C-C-H ratio with age. The ratio on the C130 was characterized by a large variability and ranged between 0.03-0.2 for plume samples and 0.06-0.2 for background samples."

The ratio on board the C130 was characterized by a large variability and it ranged between 0.03-0.2 for plume samples and 0.06-0.2 for background samples. These results are added to the text. Sentence at P6635 line 1-3 is omitted. CCN data are not presented in this study and the sentence at P6634 line 13 is reformulated.

5. We agree with the reviewer that refining the discussion section requires modifications of the conclusion paragraph. Organic nitrates are added to the list of species that were below detection limit. The similarity between SIMAT and Altzomoni are further discussed at P6635 line 21. The conclusions about in plume and out of plume results, as well as the conclusions about the oxidized functional group concentration are expanded.

Specific comments

P 6620 line 23: Grutter et al 2008 and de Foy et al 2007 are added to the text.

P6622 line 13: sentence describing sampling time is clarified.

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P6622 line 2: Rappenglueck et al 2007 is replaced by Baumgardner et al. 2009. Sentence at line 2-4 is refined to better describe the transport pattern at Altzomoni.

Coordinates of SIMAT are corrected and Fig. 1b updated.

MIRAGE is now defined at P6621 line 5 “, and MIRAGE (Megacities Impact on Regional and Global Environment)” P6621 line 19 MILAGRO is replaced by MIRAGE.

Figure 7 is modified to zoom into the area around Mexico City.

The characteristics of the two volcanoes are added to the text at P 6621 line 26 and Crounse et al. has been added to the references.

Sentence at P6634 line 6 is reformulated.

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