

***Interactive comment on* “Low molecular weight organic acids in aerosol particles from Rondônia, Brazil, during the biomass-burning, transition and wet periods” by A. H. Falkovich et al.**

A. H. Falkovich et al.

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We thank both reviewers for the detailed comments and the thoughtful reviews. To emphasize that this paper is a part of a larger field project that has produced many related results on biomass burning aerosol and their composition and climatic effects, we have added a general description of the SMOCC project in the introduction section, and references to other related articles in the results section. Below are the answers to the comments raised by the reviewers.

Specific comment:

Anonymous Referee #1

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General comments

a) With that said, the reviewer found that although the results may have reaffirmed some properties of smoke aerosols, most of the findings have been reported before.

We are in disagreement with the reviewer on this issue. The results reported here are unique in several aspects: ¶ The period analyzed represents the whole transition from heavy fires to the onset of the wet season, characterized by clean conditions ¶ Data from different samplers is reported ¶ Distribution of the chemical composition as a function of aerosol size is reported for the aerosols for the different periods ¶ Complementary data will follow in subsequent publications that provide the most comprehensive data set obtained so far on biomass burning aerosol in Brazil

b) It seems that no major insight was obtained from the size-dependent concentration information. The authors need to explain to what extent the size dependent concentration information has improved our understanding of the smoke aerosols, and whether it is crucial to have this type of measurement included in future studies. May be a simple fine-coarse division will suffice?

The size-segregated composition data appearing here for the first time is vital for models predicting the effect of biomass burning aerosols on the climate. Simple fine-coarse division is not enough as size-segregated data provides the changes in the distribution of the water soluble species in the different periods, allows to see contributions from different sources, and to observe correlations between different chemical species. Such information cannot be obtained from a simple fine-coarse division.

c) Several other important pieces of information, namely, the total water soluble organic carbon, and total mass, were not explicitly reported.

The total mass is reported in tables 3 and 4. WSOC was measured only for HiVol samples. Since the results obtained from HiVol samples are not reported due to possible sampling artifacts, as explained in section 3.3, WSOC was not explicitly reported.

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d) Possible measurement problems were not discussed in detail, including particle bouncing and interferences from gas phase species for both organic and inorganic compounds.

The problem of artifacts in aerosol sampling by these techniques has been discussed thoroughly in the literature. A paper which specifically addresses these issues and compares the results of different samplers employed in the SMOCC campaign is under preparation by Decesari et al. (Decesari, S., Fuzzi, S., Maenhaut, W., Tagliavini, E., Falkovich, A.H., Rudich, Y., Guyon, P., Mayol-Bracero, O., Fisch, G., Claeys, M., and Artaxo, P., (in preparation). Inorganic and Organic Composition of Size-Segregated Aerosols in the Dry-to-Wet Season Transition) .

Specific comments

1. 6869, line25: The term "ionic strength" has a specific definition, and is misused in this manuscript.

We have changed "High ionic strength" to "highly dissociated" throughout the paper.

2. 6876, 29: Since the WSOC concentration was used to gauge the importance of the individual organic ionic species, a description should be given to let the readers know how the WSOC was determined.

The following paragraph was added to the experimental section: "Aerosol mass concentration (Particulate Mass - PM) and Water Soluble Organic Carbon (WSOC) determination Organic carbon, elemental carbon and water-soluble organic carbon (WSOC) in the aerosol were determined by the Department of Analytical Chemistry, Institute for Nuclear Sciences, Ghent University. The detailed technique is published elsewhere [Hitzenberger, 2001; Chi, in preparation]."

3. 6872, 15: The typical sampling time of the each sampling systems should be spelled out here.

The typical sampling time is reported for all samplers in the experimental section (pg.

8872 line 12). The sentence: “Sampling times are similar for all samplers” was added to clarify that there is no need to specify the sampling time individually for every sampler, as all samplings were done more or less in parallel.

4. 6873, 20: The identities of the ion standards should be given; they are more important than the names of the manufacturers.

The relevant information was added.

5. 6875, 10: What is the "complementary information"? Spell it out. Otherwise, it sounds like a mystery.

We have changed the sentence. Now it reads: “Additional information on the inorganic and organic - both ionic and neutral - composition of bulk and size-resolved aerosols sampled during the burning period and dry-to-wet season transition appears in further publications relating to the SMOCC campaign [Maenhaut et al., 2004; Trebs et al., 2005; Schkolnik, in press; Decesari, in preparation; Decesari, in preparation; Claeys, In preparation].” Especially the four last publications in this list will contain additional information related to this paper.

6. 6876, 22: What is the acronym "IFUSP"?

We added the IFUSP acronym in the list of authors and elaborated in the mentioned line.

7. 6877, 12: Unless I missed it, how are the PM concentrations determined for each size bin? And in this regard, Figure 6 's y-axis label ΔC should be ΔC_i .

Concerning Figure 6, we have changed the figure according to the reviewer's request. Concerning PM determination, the following sentence was added to the experimental section: “Aerosol mass concentrations were determined for each size bin in the SFU and MOUDI samples. It was measured gravimetrically in a Metler electronic microbalance with 1 microgram sensitivity. Before weighing, the Nuclepore filters were left for 24 hours under radioactive sources for static electricity removal, and under a constant

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temperature of 18°C and 50% relative humidity. Each filter was weighed 3 times on different days, and the average of the three masses reported. The air volume through the filters was measured using precision mass flowmeters.”

8. 6878, 8: Is there a possibility that the Na and Cl observed were due to contamination as they don't have major known sources other than the sea-salt aerosols?

Contamination can definitely be excluded. We looked closely at the data for the coarse filters of the UGent RNN SFU samples. The percentage ratio (coarse Na)/(coarse PM) is clearly systematically higher for the daytime than for the nighttime samples. Based on 29 daytime samples, the percentage of coarse Na in the coarse PM is as follows: Mean \pm std.dev: 2.72 \pm 2.02 Median (min - max): 2.61 (0.20 - 8.13) For the 28 nighttime samples, the percentage of coarse Na in the coarse PM is as follows: Mean \pm std.dev: 0.64 \pm 0.49 Median (min - max): 0.48 (0.07 - 1.58) It might be that the Na is indeed aged sea salt that is transported to the FNS site above the boundary layer. During the daytime that aged sea salt can mix down to the boundary layer, but during the night not really. Additional evidence to the authenticity of the NaCl measured is given in the following sentence, which was added to the relevant section: “During sampling a 20 mm rain event occurred, an unusual event for the dry season in Amazonia. The Cl-molar concentration in a rainwater sample collected on the same day, and analyzed by the IFUSP group, was equal to that of Na⁺, indicating the presence of NaCl in the rainwater. The Cl⁻ concentration in the rainwater sample (200 μ g/L) was almost as high as the SO₄²⁻ concentration (230 μ g/L) [Domingues M., Artaxo P., unpublished results]” A paragraph was added to the discussion section to elaborate further indications that the Na and Cl in the sample did not arise from contamination. “An increase in PM and high Na⁺ and Cl⁻ concentrations observed in the coarse mode of sample MDRO40, coincided with a short rain event. The equal Na⁺ and Cl⁻ molar concentration in a rainwater sample collected on the same day may indicate the presence of aged sea salt in the rainwater. However, penetration of marine air masses to the sampling area seems improbable. Even if air masses from the Atlantic reached the Rondônia region, most of

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the marine aerosols would be wet-deposited during the several days of transport. We currently do not have a good explanation for the presence of NaCl in these samples.”

9. 6879, 5: Since no denuders were used in any of the sampling systems, the authors need to address the possible interference from gas phase species. For example, the high NO₃- level associated with the large particles might be caused by the absorption of gaseous HNO₃. In this regard, the readers also need to know if the WSOC measurement might suffer from gas phase interference which could result in an underestimate of the fraction of the ionic organic components. For technical reasons, a denuder that was planned to be used in the field campaign was not available. Therefore, the only way to check interferences from gas-phase species was through back to front filter ratios. And indeed, HiVol results were not reported in the paper due to high concentrations of HNO₃ and oxalate on the back filters. Such an effect was not found for the SFU and MOUDI samples. The discussion of this point appears in the HiVol section in the paper.

10. 6880, 24: The statement "indicating that the fine aerosols consist mainly of smoke particles." is not necessarily true. It is more correct to state the other way around, namely, that the smoke particles are all confined in the fine PM fraction. Imaging if the original statement is true, then no particle is present if there is no vegetation burning.

The word “mainly” was deliberately used to indicate that there might be other sources for FPM, but that they are small. Additionally, while it cannot be deduced from the cluster analysis that “the smoke particles are all confined in the fine PM fraction” (this is separately deduced from the size-segregated analysis), we believe that our conclusion is valid: if FPM follows the same emission pattern as fine K⁺, which is itself emitted primarily from smoke, it means that FPM is also emitted primarily (not solely) from smoke. Had FPM not been emitted primarily from smoke, it wouldn't have followed the smoke and thus the K⁺, emission pattern. The similarity of size distribution and time-trends of PM to that of levoglucosan, shown in another work [Schkolnik, ES&T, in press] also indicates the strong biomass burning source of PM. The sentence: “as

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was further supported by the size distributions and temporal behavior of levoglucosan, a specific biomass burning tracer, in a related paper [Schkolnik, ES&T, in press].” Was added to the relevant section.

11. 6881, 3: The reviewer doesn’t understand why the closeness between C3-C6 DCA and (NH₄)₂SO₄ suggests that they are derived from vegetation combustion.

The sentence was changed to: “The recently published size-resolved measurements of episodes of elevated LMW DCA concentrations due to biomass burning plumes passing over the measurement site [Jaffrezo et al., 1998; Ma et al., 2003], have shown that the size distributions of K and DCA were skewed toward the accumulation mode and exhibited the very same shape as sulfate’s, suggesting internal mixing of these species in the same particles. Thus, considering the proximity of the DCA C3-C6 cluster to the ammonium sulfate cluster (Fig.9), the similarity of their size distribution to that of SO₄⁻ and NH₄⁺ (Fig. 6 a, b), and their proximity to the PM and K⁺ cluster, we suggest that they have a strong common source, i.e., vegetation combustion [Jaffrezo et al., 1998; Ma et al., ,2003].”

12. 6881, 15: The sentence here is merely repeating the observation, not offering scientific explanations. Could it be that the black carbon accounts for the missing mass in the smaller size particles? Does this fraction change as a function of time or age?

Black carbon accounts for only a small fraction of the mass (certainly less than 10%; also in the fine particles). However, in order to make the sentence more coherent, we have changed it to: “In the dry period (Figure 6a-c), PM and most of the ion size distributions exhibit a maximum between 0.33-0.56 μm. In a related paper, Decesari et al. show that in this size-bin all species show a peak [Decesari, in preparation]. Considering this, the peak of the total ionic mass to PM ratio between 0.56-1.0 μm in Figure 7a indicates that other species, unaccounted for in this work, dominate the 0.33-0.56 μm size-bin.”

13. 6881, 19: C2-C6 should read C3-C6?

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No, it shouldn't. In this case we include oxalic acid (=C2).

14. 6882, 1-19: not much is new in this section. In fact, one needs to eliminate the possibility of the gaseous HNO₃ interference first.

Please see the reply to comment 9.

15. 6882, 17: This sentence is entirely confusing. First, what is the loss-free technique used to determine the NO₃-? And if it offers the true quantitation of NO₃- (which showed that NO₃- was greater than SO₄²⁻), then the results reported in this manuscript showing SO₄²⁻ being greater than NO₃- must be erroneous.

Since this sentence deals with another work, which we refer to in the related papers list, we removed the sentence from the paper.

16. 6883, 5: If levoglucosan was also measured, the authors should have investigated its relationship with K, and the usefulness of both as biomass burning tracers. This should be very valuable.

This discussion appears in the Schkolnik et al. paper, which is referred to in this very line.

17. 6883, 10: The authors need to explain why crustal material derived aerosols are more prevalent during the wet season than dry season. The rain during the wet season should lesson the chance of wind blown dust and the dry season should make dust contribution more important especially with the aid of turbulence caused by fire events.

There is no claim that there are more crustal emissions during the wet period, but that the crustal emissions are more dominant during the wet period, because during the dry period smoke emission is so intense, that it practically masks the crustal emissions.

To be more specific, in the fine, coarse, and PM₁₀ size fractions, the concentration of the crustal component (expressed in $\mu\text{g}/\text{m}^3$) is clearly highest in the dry period and lowest in the wet period. The same is true for the PM concentration. Furthermore,

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the fraction of the PM that is attributable to the crustal component does not vary much from period to period. About 10% of the PM in the PM10 size fraction comes from crustal material in each of the 3 periods. What changes greatly with period is the Coarse/Fine ratio for the PM. This means that in the wet season, the biomass burning component (including mineral dust that is associated with the fires) becomes much less important. The "background" biogenic+biological aerosol, which is mainly associated with the coarse size fraction becomes then more important in a RELATIVE sense (not in terms of air concentrations, but relative to the smoke aerosol). Summarizing, we can say that 1. During the dry period we have mostly smoke aerosol (including mineral dust associated with the fires), which is mostly associated with the small size fraction, and on top of that we have "background" biogenic+biological+mineral dust aerosol, which is mainly associated with the coarse size fraction. 2. During the wet period, the "background" biogenic+biological+mineral dust aerosol, although probably present in lower atmospheric concentration than during the dry period, becomes the dominant component, and is then much more important than the smoke aerosol.

18. 6884, 22: Using words like "sophisticated" doesn't mean much, why not tell the readers the name/principle of the technique.

The sentence: "Using a high-volume air sampler and an annular denuder sampling system with a Na₂CO₃ coated denuder to trap gaseous organic acids and a Na₂CO₃ impregnated quartz fiber filter to collect particles" was added to the relevant section.

19. 6886, 10: change "compositional data" to "composition data".

The term was changed throughout the paper.

20. 6904, Figure 6: It is not possible to discern the size-dependence of the ionic species as plotted in Fig. 6. In order to reveal the size dependence patterns of each species, they should be plotted individually. The reviewer cannot be convinced by Fig. 6 that, for example, the aromatic carboxylic acid has the same size dependence as that of K.

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We changed the figures so that it will be easier to discern the different species.

21, 6886: This conclusion section is basically a very generalized discussion which doesn't even rely upon the data reported in this work. Perhaps the authors don't want to repeat what they have already said in the abstract?

The second paragraph of the conclusion section was moved to the end of the discussion section. Main findings were further repeated in the conclusions section.

22, 6897: Acetate is misspelled.

It has been corrected.

Anonymous Referee #2

General comment: It would be interesting to know whether there is also a study under way that gives more detailed information about the composition of the neutral fraction of these aerosols.

A sentence was added to the results section: "Additional information on the inorganic and organic - both ionic and neutral - composition of bulk and size-resolved aerosols sampled during the burning period and dry-to-wet season transition appears in further publications relating to SMOCC [Maenhaut et al., 2004; Trebs et al., 2005; Schkolnik, in press; Decesari, in preparation; Decesari, in preparation; Claeys, In preparation]." Information about the neutral fraction of the aerosol can be found in the Schkolnik et al. paper, in both of the Decesari et al. papers and in the Claeys et al. paper.

Specific comments: 1) The paper gives very detailed data for the ions. However, the overall composition of the aerosol is not further specified. It would be interesting to have some information about the size resolved water-soluble and water-insoluble organic carbon concentrations (e.g. in Tables 3 and/or 4).

Tables 3 and 4 show results obtained from SFU and MOUDI samplers. We have WSOC and OC data only for the HiVol sampler. These samplers were operated with a 6hr

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phase between them. Since emission levels varied diurnally, it is hard to compare between their results, and therefore OC and WSOC were not reported. The Decesari's planned ACP manuscript, will contain some of this information.

2) Section 4.1: Cluster analysis: Semivolatile and non-volatile species are included in the cluster analysis. A correlation between non-volatile species seems to have quite different implications than a correlation of semivolatile species with other semivolatile or non-volatile ones. A more explicit discussion of the observed correlations with respect to the volatility of the correlating species would therefore be useful.

We have surveyed only correlations with PM to check association as primary or secondary compounds. The conclusions from the cluster analysis (with this specific aim) are further corroborated by the results of the size distributions of the chemical species, which are very similar for PM, K, DCA, oxalate, SO₄, NH₄ and NO₃. The highly volatile formic and acetic acids can indeed be found on the most distant cluster in the analysis, demonstrating the difference between volatile and semi-volatile organics.

3) Section 4.3, abstract and conclusion: semivolatility of dicarboxylic acids: The authors seem to imply that the only evidence of dicarboxylic acids in the gas phase comes from front/back filter ratios. However, there are several works that directly sampled the gas phase and found considerable dicarboxylic acid concentrations in this fraction (Baboukas et al., 2000; Kavouras and Stephanou, 2002, Sellegri et al., 2003). To conclude whether the dicarboxylic acids are confined to the particulate phase, these species should be sampled in the gas and in the particulate phase in a way that excludes revolatilization. The sentences stating that the dicarboxylic acids are confined to the particulate phase should therefore be removed or modified. One important factor that influences the gas / particle partitioning of acids is the acidity of the aerosol particles. In neutral or even alkaline particles, the effective Henry's law constant is higher than in acidic ones. While the Rondonian aerosol particles are neutral or even alkaline, rural background sites aerosol particles are usually acidic. Since Limbeck et al. (2001) sampled at a rural background site, this might explain the different findings of the two

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studies.

The point raised by the referee is well taken. We now state that the differences can arise from difference in aerosol chemical composition and acidity. We added these sentences to the relevant section: "Our sampling intervals were shorter (about 12 hours) except for five transition period samples, which were collected for 24-36 hours. Loaded filters were immediately placed in a freezer (-25oC) and thus stored until analysis. Additional possible difference between the two samples can arise from different particles acidity. Rondônia particles are neutral or slightly basic. "We have not found evidence for semi-volatility of DCA, and conclude that they are confined to the aerosol phase in this case. This conclusion is in line with studies by Saxena and Hildemann [1996]."

4) Page 6881, lines 12 - 18: Does the discrepancy between Figures 6 and 7 not just reflect a larger ratio of ions / PM in the 0.56 - 1.0 micron size bin compared with the 0.33 - 0.56 micron size bin?

Please see our reply to referee #1 comment #12.

Technical comments:

Page 6870, line 24: it is not clear from the context what is meant by simple aliphatic acids: mono- and dicarboxylic or only dicarboxylic acids?

For clarification, the sentence was modified: "The simple di- and tricarboxylic aliphatic acids were found to make up only about 1-2% of the WSOC ".

Page 6872, line 10: should it be Kirkman et al. (2002)?

We have corrected this.

Figure 1: the oxalate and nitrate concentrations are hardly visible in this Figure.

The figure was improved.

Figure 6: In some plots, the concentrations of only some ions are visible (e.g. in Figure

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6a, the concentration of K^+ is only visible in two size fractions, the one of NH_4^+ only in three). This should be improved.

The figure was improved.

Figure 8: should it be FPM instead of PM (below K^+)?

In the text it is stated that all the components in the dendogram are in the fine fraction. However, we have also added this information to the figure caption.

The typographic errors were corrected according to the referee's suggestion.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6867, 2004.

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