MS No.: acp-2011-441, J. Schneider et al.

Reply to Reviewer 2

General remark: The reviewer refers to line numbers that don't match the published ACPD version of the manuscript. Thus we assume that she/he refers to the submitted version which had been slightly revised before publication in ACPD.

Reviewers Comment:

Aside from minor questions detailed below, my two general concerns with this manuscript (in this form) are that

(1) the bulk of the text appears to be focused on the method, while only the most basic results are presented in the remaining portion

and (2) the finding from the Chen 2009 already concluded that PBAP was a low fraction of OM. From the abstract and title, it seems that the authors are more focused on the findings rather than the method, but the length of interpretation and discussion does not really mirror that goal. I find at most one page on the contributions of each biological marker to the total OM with little discussion beyond the observation that most of the OM was likely secondary. For publication, I would like to see the authors either retarget the title, abstract, and conclusions to make the goal of the paper (as is) more clear. That is, developing a method to identify and quantify PBAPs in pristine conditions OR I would like to see a more thorough analysis and discussion of the results, with additional references if possible and appropriate. This would entail describing how the Chen 2009 study is complemented, and not repeated, by this one.

Our reply:

The main goal of this paper is to present a method developed to identify and quantify PBAP using AMS data. We also think it is important to show the application to real field data when presenting a new method.
The low fraction of PBAP to submicron organic aerosol reported in Chen et al. (2009) are based on our data obtained by this method, therefore the results are referenced in Chen et al. as "J. Schneider, unpublished data". Our results were also mentioned in Martin et al., ACP (2010), and Pöschl et al., Science (2010) with reference to Chen et al. (2009). The present paper is therefore necessary to explain the method in detail that led to those results on PBAP.

However, we agree to change the title and suggest: „Mass-spectrometric identification of primary biological particle markers and application to pristine submicron aerosol measurements in Amazonia“

Thereby we will emphasize that the method is the main focus of the paper. We will also modify the abstract and the conclusions accordingly.

Detailed Comments:

Line 24: Here and throughout the authors refer to their value as "upper limits" on the PBAP contribution. However, I wonder how likely it is that some components are not captured by the key markers used and therefore the calculated values are simply "estimates" rather than "limits." Aside

from the fact that 2/3 of the cell are carbohydrates or proteins, I wonder if the authors have any other more quantitative reason to believe they have a true upper limit.

> We use the term "upper limits" because it is likely that other organic aerosol components might contribute to the chosen markers (e.g., biomass burning also produces m/z 60 and 73). Also, we were not able to find applicable background values. Thus we think it is more likely that our results overestimate the actual contribution of PBAP. See also points 3 and 6 in the reply to reviewer 1.

Line 30: Where did this 20% come from? Is it from 7.5%+5.6% and rounded up to 20%? It's a bit difficult to follow since the preceding sentence says the method captures 2/3 of the contents, then an upper limit is introduced. If a rounding up was done, then it should be more explicit since 13.1% is not all that close to 20%.

> Proteins and carbohydrates account for approximately 2/3 of the mass fraction of a biological cell. Therefore we multiply the 13.1% by 3/2 which yields approximately 20%.
> See also comment 6 of reviewer 1 and our reply.

Line 36: Is this (30%) the highest average number fraction reported, or is this a median value? Given that your results are in conflict with a number fraction this high, it would be better to provide the range of observed number fractions (and their environments), especially if the goal of this study is to refute the significant contribution of PBAPs to submicron aerosol previously reported. Further, the discussion mentions this 30% and claims it is not in agreement with the finding that 20% or less by pass was primary. Did any other studies find number fractions in agreement with the current study? If none in agreement are reported, the authors need a stronger case that their results are truly upper limits, and not estimates.

> First, we have to emphasize here that the 30% are number fraction in the submicron range and that our 20% are mass fraction in the submicron range. Since PBAP are expected to be rather large, a submicron number fraction of 30% would lead to a much higher submicron mass fraction.
> To our knowledge only the studies by Jaenicke and co-workers report number fractions of PBAP in the submicron range. Only in the paper by Matthias-Maser and Jaenicke (1995) size resolved number fraction are reported, from which we calculated the submicron number fraction that we reported. The value of 30% is an average, the data reported by Matthias-Maser and Jaenicke range between 12 and 53%.

Line 60: It would be helpful to add some information regarding the potential role of the current study address how important PBAPs are to IN in the Amazon.

> PBAP are mainly found in the supermicron size range. However, submicron particles are much more efficiently transported into the free troposphere (where temperatures are low enough to allow ice formation). Thus it is important to know whether there are submicron PBAP because PBAP usually are efficient IN. We will include this statement in the revised version of the manuscript.

Line 73: Was number fraction of PBAPs measured and published? If so, it should be added to the discussion with a comparison to mass fraction. If not, please indicate when and from whom these results will be available. If they will never be available, then it should be mentioned that it was not measured, and it should be omitted as one of the research goals.

> Number fraction of PBAP was measured in the supermicron size range by a UV-APS (Group U. Pöschl, Biogeochmistry Dept., MPIC Mainz, see overview table in Martin et al. (2010)). These data have yet to be published, but since the measurements were a research goal of AMAZE and are related to the current study they are mentioned here.

Line 76: What fraction of IN were PBAPs?

> This is answered by Prenni et al. (2010), where the authors report from the AMAZE-08 study: "At temperatures warmer than about 25°C, biological particles seem to dominate the ice-nucleus population, although ice-nucleus number concentrations are only of the order of 1-2 per litre at these temperatures. These ice nuclei will be the first to initiate ice formation in clouds, and thus despite their low number concentrations, primary biological aerosol particles will have an important role in precipitation and cloud dynamics. At temperatures colder than 27°C, dust becomes increasingly more important, with ice-nucleus number directly tied to dust number concentrations."

Line 197: Again, it is unclear whether an estimate or a limit was determined.

> See comment above, which clarifies why giving upper limits is justified.

Section 2.2: What other measurements are available for this campaign? A reference is given for the campaign but it would be useful for readers to know whether other valuable information is available or not before searching for the cited work.

> On page 11419 and 11420 of the given reference (Martin et al., (2010), same special issue) a very long and detailed table is included that lists all available measurements. We feel that repeating the table here would not make sense since it is too long. We will include a sentence here stating that a complete overview of the measurements performed during AMAZE-08 is given in Martin et al. (2010).

Line 253: The SF is introduced here, so it would be more fitting to provide equation 3.1 here in the methods, rather than in the Results. In fact, it is unclear that any of the text between lines 342 and 358 belong in the results section. It may fit better just before section 3.2

> We moved lines 342-358 including Equ. 3.1 into the methods section

Lines 338-341: If a previous study has already shown secondary sources to dominate submicron OM, does that make the finding here redundant? The title implies the low abundance is a new finding: : :. If the finding here is the same as a previously published work, both using AMS, then the focus of this paper should really be on the mass spectrometric method of identifying PBAPs since there is not a new conclusion being drawn here. Did the previous study leave unanswered questions that this study aims to address? That should be stated up front in the introduction.

> As already explained above, the results on PBAP in Chen et al. (2010) are from the same study. The results were reported there as "J. Schneider, unpublished data", and further mentioned in Martin et al. (2010) and Pöschl et al. (2010) with reference to Chen et al. (2009). Thus the present paper is not redundant but describes in detail the method that was used to obtain these results. We agree that we have to emphasize from the beginning that the focus of the present paper is the method.

Line 404: The data for this spike event show no increase in the preceding or following measurements, and the two are quite similar to one another. Is there any possibility that the rain event contaminated the sampling conditions in any way? Since the authors have no good explanation for this spike, and since the bounding measurements are not evaluated, the authors should address whether this could be an artifact instead of a real "event."

> This is of course another explanation that we will consider. However, also this will remain speculative.

Figure 3: Consider a log or split axis on the left to allow the detail of the majority of values to be seen.

This is a good point, we will use a log axis in the revised version of the Figure.

Minor Issues:

Line 28: This is slightly awkward. Consider revising as, "Carbohydrates and proteins (amino acids) compose approximately two-thirds of the dry mass: : :"

Changed to "Carbohydrates and proteins (composed of amino acids) make up for…"

Line 30: Add " in this campaign" or "measured here" or some other text to avoid generalizing the findings here to all other pristine cases.

Changed to "Thus, our findings suggest an upper limit for the PBAPs mass fraction of about 20% to the submicron organic aerosol measured in Amazonia during AMAZE-08."

Line 59: Insert a comma after "emissions"

corrected

Line 60: Insert a space between "such" and "important"

Corrected (already in the published ACPD version)

Lines 61-64: Slightly awkward, reword to be more direct. Split into two sentences to avoid a run-on.

Changed into: "Another important effect is that PBAP for certain meteorological conditions can take up enough water to act as "giant" cloud condensation nuclei. Such "giant" CCN generate larger droplets that fall faster than droplets formed from smaller CCN, thereby facilitating coalescence and warm rain formation (Möhler et al., 2007)."

Line 9: Remove plural on "spectrometers"

We assume this refers to line 93 ? - corrected

Line 132: Insert a space between "chains" and "as"

Corrected (already in the published ACPD version)

Line 194: Omit second period.

Corrected (already in the published ACPD version)

Line 384: Provide the confidence level of the significance test (95% is assumed otherwise).

The statement refers to the one-sigma (68%) confidence level.

References

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