Reply to Reviewer 1

Reviewer's comment:

1. Free amino acids have been found in atmospheric precipitation, cloud water droplets, and aerosols (Mopper and Zika, Nature, 1987) (Matsumoto and Uematsu, Atmos. Environ., 2005). …. This is only a minor point if the authors suggest that 20% of submicron aerosol is attributed to bacteria and viruses in the atmosphere.

> Our reply:
>
> We cannot distinguish between free amino acids and amino acids from PBAP. Free amino acids are thought to originate from PBAP as well (Matsumoto and Uematsu, 2005). Thus, free amino acids would only affect our results if they would origin from supermicron PBAP and would then be transferred via gas-phase processes into submicron aerosol particles. Such a process appears unlikely. Thus, this appears to be irrelevant for our analysis.
>
> In the revised version we will clarify that our analysis includes amino acids from submicron PBAP as well as free amino acids in submicron aerosol.

2. In calculating the scaling factor for the amino acid class, the authors chose not to include glycine and tryptophan. However, glycine has been found to be the most or second---most abundant amino acid in ambient PM2.5 aerosol, fog---water, and rain---water samples (Zhang and Anastasio, Atmos. Environ., 2003) (Milne and Zitke, J. Atmos. Chem., 1993). Using an average scaling factor that excludes glycine (as well as tryptophan) appears to not accurately describe the amino acids present in the atmosphere. The authors should consider including a range for the scaling factor that both includes and excludes glycine and tryptophan. In addition the authors should consider using a weighted average for the scaling factor for amino acids that would more accurately describe the distribution of amino acids found in the atmosphere and/or bacteria and viruses.

> Glycine is the only amino acid (the smallest one) where the loss of the COOH group yields the marker ion CH_4N^+ directly. Thus, we think that including glycine in this average would overestimate the influence of glycine.
>
> Similarly, there are only two hetero-aromatic amino acids among the 20 proteinogenic amino acids, namely tryptophane and histidine, where upon fragmentation and and ionization the positive charge remains on the stable hetero-aromatic ring structure and therefore yield lower intensities of CH_4N^+ and $C_2H_4N^+$.
>
> Thus we think that the remaining six investigated amino acids are a good proxy for the majority of the proteinogenic amino acids because of similar structures.
>
> We will discuss this issue in the revised version of the manuscript.

3. The upper limits of the fractions of amino acids and carbohydrates were calculated as: …... However, the authors used a value of 0 to describe $f_{i,background}$, even though background values for other campaigns were presented in the manuscript. Since background values are known for some

regions, including this information into the calculation could produce at most, a lower bound for the percentage of PBAP in the Amazon Rainforest.

> We would very much like to include a background value, because in our opinion the upper limit for carbohydrate is too high (see point 6 below). However, the known background values are not applicable here in the pristine conditions in Amazonia. For example, if we apply the suggested value f_{60} of 0.003 by Cubison et al. (2011), the resulting carbohydrate concentrations are around zero.

> Thus, in our case it seems to be more appropriate to report an upper limit instead of using non-applicable background values.

4. On page 19158, the authors state that the carbohydrate fraction peaked during the night on multiple occasions. According to this manuscript and Chen et al., 2009, the remaining organic aerosol presented here is primarily biogenic SOA. Since the biogenic SOA had a diel pattern (Chen et al., GRL, 2009), which peaked during the day due to photochemical production, is the increase in PBAP at night due to a decrease in photochemical biogenic SOA production?

> The reviewer's suggestion is certainly a possible explanation for our findings. The diel pattern of biogenic SOA shown in Chen et al. (2009) would lead to a higher fraction of carbohydrates during night-time if the absolute concentration of carbohydrates would remain approximately constant. But, in this case the amino acid markers should show the same behavior which they clearly do not. Thus, this explanation seems to be unlikely. But we will include it in the discussion of the findings.

5. The authors describe submicron PBAP as primarily bacteria and viruses. Vegetative detritus has been found to be a constituent of fine organic aerosol (Rogge et al., Environ. Sci. Technol., 1993). Do the authors feel vegetative detritus and vegetative matter from wind---blown leaf abrasions do not attribute to the organic mass of submicron aerosols?

> We were not aware of this reference. Rogge et al. (1993) report that "contemporary" carbon makes up between 23 and 52% of fine mode aerosol. This contemporary carbon consists not only of vegetative detritus but also of meat cooking, fireplace combustion of wood, cigarette smoke, road dust, and the natural rubber or resin content of vehicle tire wear debris. Based on these results the contribution of vegetative detritus seems to be more in the order of 10% or below. We will mention this in the revised version.

6. On page 19160, the authors claim, "Because amino acids in the form of proteins and carbohydrates together account for about 2/3 of a biological cell (Munk, 2000), we can conclude that the upper limit of the total contribution of PBAPs to the submicron organic mass concentration was no more than 20%." It appears that the authors calculated the PBAP organic mass contribution as follows: ………When the correct apportionment of protein and carbohydrates are considered (.50 and .15) with the ambient fractions (.075 and .056), the actual upper bound of PBAP should be 52% and not 20%.

We disagree with the referee's calculation. His Equ. 3 should read:

$$f_{B,A} = f_{P,A}/f_{P,B} = f_{C,A}/f_{C,B},$$

because both approaches (either regarding only amino acids/proteins or carbohydrates) should arrive at the same percentage. They would, if the measured ratio would equal the ratio Φ in the cells.

However, the fact that is does not is most likely because the carbohydrates are overestimated (see discussion on background subtraction in point 3). Considering the amino acids alone, we would derive an upper limit ($f_{P,A}/f_{P,B}$) of $0.075/0.5 = 0.15$ (15%). Considering only carbohydrates, we would get $0.056/0.15 = 0.37$ (37%). The large discrepancy in the ratio carbohydrates/ proteins in cells (Φ) and the measured ratio carbohydrates/amino acids suggests that the carbohydrate upper limit is somewhat too high, due to other sources (as biomass burning for levoglucosan) that would have to be corrected by background subtraction if appropriate values were available.

Additionally, as the overview in our introduction shows, the ratio Φ in cells is not necessarily constant at 0.15/0.5, but may vary considerably, because the protein percentage may range from 10 to 68%, and the carbohydrates can range from 8 to 55%.

We will discuss these uncertainties in more detail in the revised version of the paper.

Specific comments:

1. Page 19151, Line 18: What was the justification for averaging over 12 hours?

12 hours were chosen because

a) a sufficient long time is needed for the high resolution analysis (at the low mass concentration in Amazonia) and

b) 12 hours allow for a day/night differentiation.

2. Page 19161, Lines 3---5: Sentence appears to be out of context. Consider removing or moving to a different section.

This sentence is meant to back up the low mass fraction of PBAP found in submicron aerosol, also at rural sites. To make this more clear, we changed the sentence into: "Another study from a completely different location (urban, suburban, and rural sites in Norway) that investigated the content of sugar and sugar alcohols in $PM_{2.5}$ (Yttri et al., 2007), also found that the sum of sugars and sugar-alcohols contributed only by a small fraction (0.2% to 1.0% by mass) to organic carbon in $PM_{2.5}$."

References

Chen, Q., D. K. Farmer, J. Schneider, S. R. Zorn, C. L. Heald, T. G. Karl, A. Guenther, J. D. Allan, N. Robinson, H. Coe, J. R. Kimmel, T. Pauliquevis, S. Borrmann, U. Poschl, M. O. Andreae, P. Artaxo, J. L. Jimenez, and S. T. Martin: Mass spectral characterization of submicron biogenic organic particles in the Amazon Basin, Geophys. Res. Lett., 36, L20806, doi:10.1029/2009gl039880, 2009.

Cubison, M. J., A. M. Ortega, P. L. Hayes, D. K. Farmer, D. Day, M. J. Lechner, W. H. Brune, E. Apel, G. S. Diskin, J. A. Fisher, H. E. Fuelberg, A. Hecobian, D. J. Knapp, T. Mikoviny, D. Riemer, G. W. Sachse, W. Sessions, R. J. Weber, A. J. Weinheimer, A. Wisthaler, and J. L. Jimenez: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and lab studies, Atmos. Chem. Phys. Discuss., 11, 12103-12140, doi:10.5194/acpd-11-12103-2011, 2011.

Matsumoto, K., and M. Uematsu: Free amino acids in marine aerosols over the western North Pacific Ocean, Atmos. Environ., 39, 2163-2170, doi:10.1016/j.atmosenv.2004.12.022, 2005.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit: Sources of fine organic aerosol 4. Particulate abrasion products from leaf surfaces of urban plants, Environ. Sci. Technol., 27, 2700-2711, doi:10.1021/es00049a008, 1993.

Yttri, K. E., C. Dye, and G. Kiss: Ambient aerosol concentrations of sugars and sugar-alcohols at four different sites in Norway, Atmospheric Chemistry and Physics, 7, 4267-4279, 2007.