

Primary biological aerosol particles: Detection and identification of characteristic compounds by aerosol mass spectrometry

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The contribution of primary biological aerosol (PBA) to the total aerosol particle concentration is estimated to range between 25% and 80%, depending on location and season (e.g., Matthias-Maser and Jaenicke, 1995; Jaenicke, 2005). Especially in the tropical rain forest PBA is expected to be a major fraction of aerosol particles in the supermicron range, and also an important part of the submicron aerosol. PBA particles consist of species as plant fragments, pollen, spores, fungi and viruses. Therefore, they contain a wide variety of different chemical compounds and substance classes, such as amino acids and proteins, sugars and cellulose, lipids or chlorophyll.

For this reason we have performed mass spectrometric laboratory measurements (Aerodyne C-ToF and HR-ToF AMS, single particle laser ablation instrument SPLAT) on pure submicron aerosol particles containing typical PBA compounds, such as carbohydrates and amino acids. Our aim was to identify typical mass spectral patterns of these compounds, and to explain the observed fragmentation patterns on the basis of molecular structures. In doing so, the emphasis was set on determining several typical mass spectrometric markers or patterns which would enable us to identify in ambient data these substance classes typical for PBA. Therefore, the laboratory data were compared to submicron particle mass spectra obtained during AMAZE-08 (Amazonian Aerosol Characterization Experiment, Brazil, February/March 2008). During this campaign ambient aerosol was measured with a HR-ToF AMS in the remote Brazilian rainforest, where a comparatively large amount of PBA is suspected to contribute to the total submicron organic mass.

The laboratory results indicate that characteristic m/z ratios for carbohydrates (e.g., glucose, saccharose, mannitol) can be identified, for example $m/z = 60$ ($C_2H_4O_2^+$) or $m/z = 61$ ($C_2H_5O_2^+$). For amino acids certain typical nitrogen-containing fragments were found (e.g. $m/z = 30$ from the fragment CH_4N^+), which also occur in the mass spectra of peptides and small proteins. Large proteins, however, seem to become oxidized to CO_2^+ to a large extent in the vaporization process of the

AMS, seemingly making it difficult to detect such proteins in atmospheric aerosol particles with this instrument.

The field data from AMAZE-08 were examined with respect to these markers, and their presence could be verified. The contribution of carbohydrates and of amino acids and proteins to the total organic mass for this data set is estimated to about 5% for each of both examined substance classes.

Interestingly, the typical markers of sugars are identical to those of levoglucosan, a known and commonly used marker for biomass burning. As levoglucosan is formed from burning of cellular material, this comes as no surprise, but at the same time raises the question to which extent these markers for biomass burning may be affected by PBA (and vice versa), and how the two sources can or cannot be distinguished by means of mass spectrometry alone.

Another challenge for the positive identification of carbohydrates in organic matter may arise from overlap with oxygen-containing secondary organic aerosol components, which probably could not be distinguished from PBA-related signals by mass spectrometric markers. Here, the nitrogen-containing substances seem to be a more promising approach. In high resolution mass spectra, such as obtained by the HR-ToF AMS the peaks from nitrogen-containing fragments can be well determined, and the respective markers can more clearly be contributed to PBA than it is the case with the markers for the oxygen-containing compounds, because the sources for the former fragments are much more unique. Nevertheless, the uncertainty inherent in the complete vaporization of the proteins in the AMS remains open. Thus, it is still questionable if the quantification of PBA using AMS field data can be more than a rough estimation.

Jaenicke, R. (2005), *Science*, 308, 73.

Matthias-Maser, S., and R. Jaenicke (1995), *Atm. Res.* 39, 279-286.