



Application of TD PTR-MS to the analysis of DOM from alpine snow

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The exchange of organic matter (OM) between the atmosphere and snow is poorly understood due to the limited accessibility of the remote sites and the convoluted processes of deposition and re-volatilisation. Moreover, the complex nature of OM is difficult to characterise in detail. Wet or dry deposition of organic aerosol (OA) is the main source of OM. As new OM is added to the snow, its nature and chemical composition changes due to chemical and biological processing. The final fate of this OM is either re-emission to the atmosphere, release during the melting, or burial in the glacier's ice. OM that is finally retained in the glaciers holds a valuable historical record of past atmospheric conditions. However, our understanding of the processes involving OM is insufficient to translate the measurements into an interpretation of the past atmosphere.

The aim of this work was to examine the dynamic processes of OM change happening at the alpine snow surface with the goal to interpret the processes involved in OA deposition. In order to do so, we recently developed a rapid method for small-size DOM characterisation based on Thermal Desorption – Proton Transfer Reaction – Mass Spectrometry (TD-PTR-MS). The method has been optimised to snow sample analysis, it is fast (<15 min/run), sensitive (e.g. LoD <0.0002 ng/mL for pinonic acid, LoD <0.0001 ng/mL for levoglucosan), requires a small sample size (<2 mL of water), and it provides reasonably high mass resolution data (>4500, FWHM).

Utilising the novel TD-PTR-MS method, we analysed high-altitude snow samples (Sonnblick Observatorium, AT) and discovered various compounds associated with VOC oxidation and biomass burning events. The results show an overall increasing trend in dry deposition over a period with no precipitation (20.03-01.04.2017). We also noticed four distinctive groups of ions with similar concentration trend over that time ($R^2 > 0.9$), suggesting common atmosphere chemistry processes or transport pathways. The main two groups of ions are coming from (a) surrounding forests (e.g. pinonic acid – associated with monoterpene oxidation) and (b) residential fires (levoglucosan – common biomass burning marker). Furthermore, the snow sample taken on 29th of March showed a change in the general concentration trend, consistent with a shift in wind direction, indicating different air mass origin. This is the first study using TD-PTR-MS for the analysis of OM in the snow. The method holds significant potential for investigating the processing of OA deposition in the cryosphere.