First insight in Antarctic aerosol particle composition regarding amino acids with a new HILIC-ESI-TOF-MS method

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As a pristine region, the Antarctic peninsula can be a model region for a preindustrial atmospheric environment (Hamilton, 2014) and, accordingly, give insights in climate change related processes.

A vast number of studies was conducted focussing on either organic mater (OM) on aerosol particles (AP) or possible sources of APs. The second largest fraction of Antarctic OM are likely proteins consisting of amino acids (AA), contributing massively to the global nitrogen cycle (Zhang et al., 2003) and having impact in cloud chemistry, for example by acting as cloud condensating nuclei (CCN) (Chan et al., 2005) or ice nucleating particles (INP) (Szyrmer and Zawadzki, 1997).

The oceans are an important source of APs. First, trace gases can be emitted from the oceans then are oxidized in the atmosphere and result in secondary organic aerosol particles (SOA) (Liss and Johnson 2014). Secondly, wind and wave driven physical mechanisms (e.g. bubble bursting) lead to the formation of sea-spray aerosol particles (SSA) that emit sea salt together with primary organic aerosol (POA) (Burrows et al. 2014), which is rich in OM. The molecular nature of the OM on POA, especially of the free and combined AA, and the selected transfer processes to APs, are to this day not fully understood. Recent studies show hints of biotic transformation on APs (Zeppenfeld, 2021) and net production rates of AAs due to certain bacterial strains coming from cloud water (Jaber, 2021), therefor biotransformation may also play a role for AAs on APs.

To date, chemical analysis of AAs often is provided as a sum parameter, as robust methods for their analysis in their original form on both APs and in the SML are lacking. Through sum parameters, individual differences cannot be determined and information on biotic or abiotic transfer are lacking.

Therefore, we developed a new hydrophilic interaction liquid chromatography electrospray ionization time-of-flight mass spectrometry (HILIC-ESI-TOF-MS) method, utilizing the potential of HILIC to separate more polar analytes, compared to standard LC methods.

Advantages of the developed method are not only its broad window of analytes, but also its robustness as it can be applied to both AP and seawater samples with a short sample preparation. Time consuming steps such as derivatization are not needed and MS detection can also be used to investigate nucleobases, which can be a tracer for bacterial or viral activities.

Application to field samples

During February-March 2023, the PolarChange campaign took place. This campaign was conducted around the Antarctic Peninsula, enabling to get concerted samples of APs and the sea surface microlayer (SML).

During the cruise, high volume and low volume size segregated aerosol samples were obtained, to investigate the transfer and enrichment depending on different factors.

Due to the nature of HILIC, the polar analytes show a good retention and separation from matrix components, even though for SML samples a desalting step before the measurement must be implemented.

Through this measurements, further insights can be gained on the enrichment and chemo-selective transfer of AA from the ocean to the atmosphere.

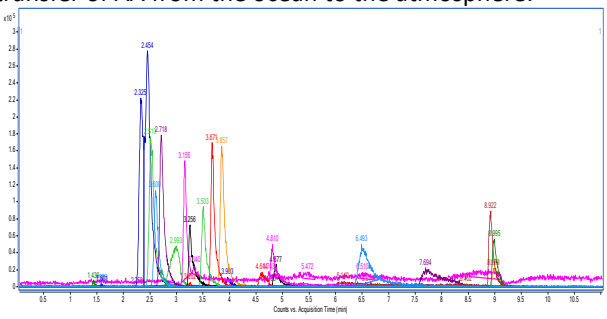

Figure 1. EICs of AA and NB obtained from a mix aqueous standard with HILIC-UHPLC-ESI-TOF-MS

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