**Development of a 2D-offline chromatographic method for the classification of HULIS carbon in atmospheric particles**

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Humic-like substances (HULIS) are a class of organic compounds found ubiquitous in fog, cloud water and atmospheric aerosols. They are named due to the similarity to terrestrial and aquatic humic substances. HULIS show a similar optical behavior and chemical complexity, but have a lower molecular weight, less aromatic properties and a higher surface activity.1-3 Currently HULIS is defined operationally by the applied extraction method (mostly solid phase extraction of aqueous particle extracts). Different established methods lead to different HULIS fractions.4,5 Together with the mostly unknown composition, results regarding HULIS are often hard to compare.

The goal of this work is to develop an offline 2D-chromatographic method combining reversed phase high performance liquid chromatography (RP-HPLC) and size-exclusion chromatography (SEC) for the fractionation of HULIS extracts. The less complex composition of the fractions will possibly lead to more detailed information about HULIS.

It´s not possible to separate HULIS using an isocratic or standard gradient RP-HPLC due to its complex composition. Using a stepwise gradient instead leads to one fraction of substances with similar polarity per gradient step. Methanol and acetonitrile were tested as organic portion of the mobile phase. Although both work, acetonitrile is favored due to is reduced background signal. The best setup is using 10 gradient steps with each increasing the acetonitrile portion every 6 minutes by 4% up to a maximum of 40%. SEC measurements show the need for using 80/20 aqueous phase/methanol as mobile phase to reduce peak fronting and increase the overall reproducibility. Additionally only a basic aqueous phase (10 mM NH4HCO3) provides a separation of the HPLC fractions. Coupling with mass spectrometry shows a clear correlation between the extracted ion chromatogram (300-1000 m/z) and the UV absorption chromatogram (diode array detector) with a total of 6 peaks with potential relevance for HULIS. Sum spectra of each peak provide first clues to the composition, but low resolution and low concentration of the samples prevent a detailed identification at the moment. These first results of method development will be presented in this contribution.

For the future it is planned to optimize the developed offline 2D-chromatography further and use higher resolution mass spectrometers to clarify the molecular composition and ideally identify some tracer molecules. Further the new method will be used to analyze samples with regional and seasonal variations to understand correlations between composition / distribution in the 2D-space (polarity, size) and the source of the particle as well as other atmospheric chemical data.

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**Literature**

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