Elucidation the composition of humic-like substances in the atmospheric aerosol via 2D liquid chromatographic fractionation and ultra-high resolution mass spectrometry

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Atmospheric aerosol particles contain a large fraction of organic carbon (OC), which contributes up to 70% of the total particle mass (Kanakidou et al. 2005). OC plays an important role for cloud formation and the earth radiative budget, as it alters microphysical properties and the ability of particles to serve as cloud condensation (Kristensen et al. 2012). Moreover, it is expected to be involved in a wide range of human health issues (Mauderly and Chow 2008). Despite its importance, only a small fraction has been identified on a molecular level, due to the high complexity with thousands of substances. OC is dominated by a class of substances often referred as humic-like substances (HULIS), which contributes up to 80% of the water-soluble organic carbon (Zheng et al. 2013). Elucidating its composition is therefore crucial to understand aerosol properties and its roll on the cloud formation process. At the same time, the high complexity of the chemically unresolved mixture is challenging.

This work shows the development of an offline two-dimensional chromatographic method, combining size exclusion (SEC) and reverse-phased chromatography (RP-HPLC), for a detailed fractionation of aerosol particle extracts. The reduced complexity of the fractions facilitates mass spectrometric (MS) analysis and leads to more detailed information about the composition of HULIS than bulk analysis. The particle extracts are separated via optimized SEC into five fraction in molar mass ranges between 160-900 g/mol. Each fraction is separated further into eleven RP-HPLC fraction with calculated octanol/water partition coefficient of 0.2-3.3, utilizing a newly developed "spiked gradient" method (Spranger et al. 2017). Heat maps of the UV-absorption at 254 nm illustrate the distribution of HULIS in the two-dimensional size-vs-polarity space (Figure 1). The distribution differs greatly depending on season and air mass input for a set of samples from Melpitz, a background station near Leipzig, Germany. In winter, the largest molecules with a relatively low polarity dominate the absorption properties, while in summer the smaller more polar one dominate.

The extensive sample treatment also improves downstream analytical techniques, like ultra-high resolution electrospray ionisation Fourier transform ion cyclotron mass spectrometry (ESI-FTIRC-MS). At least 2.5 times the amount of different molecular formulas can be assigned for the fractionated samples compared to bulk samples, mainly due to a reduction of interferences during ionisation with ESI (Noziere et al. 2015). Further, detailed information about the chemical composition are gained for each fraction. Signal distribution in Van Krevelen diagrams, the carbon oxidation state and aromaticity lead to clues regarding sources and generation processes of HULIS.
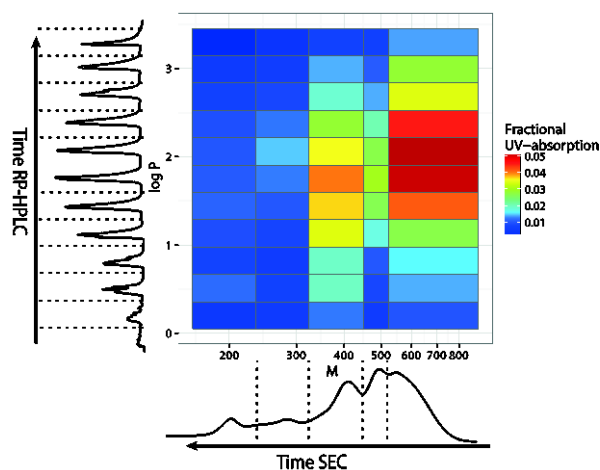

Figure 1. 2D heat map of an ambient filter sample, with the respective SEC chromatogram on the bottom and one RP-HPLC chromatogram on the left side. Dotted lines show the fraction limits.

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