Enrichment of biogenic and anthropogenic organic substances on sea spray aerosols

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Abstract

The world's oceans are the source of one of the most abundant types of natural aerosols, namely sea spray aerosols (SSA). By scattering solar radiation, SSA play a significant role in controlling the Earth's radiation budget, while they are also involved in the formation of clouds, acting as cloud condensation nuclei (CCN). To understand the connection between biogeochemical processes occurring in the ocean and in the atmosphere, it is crucial to gain better insight into the detailed chemical composition of SSA, which broadly consists of sea salt and marine organic matter. The aim of this thesis is to (1) better understand the impact of ocean biological activity on the chemical composition of SSA and (2) improve the knowledge on the ability of SSA to transport different organic pollutants to the atmosphere. In **Paper I** it was shown that changes in the composition of marine organic matter during a phytoplankton bloom in the North Atlantic were clearly reflected in the composition of generated SSA. Increased chlorophyll a concentration in seawater was correlated with the presence of lipid-like compounds with high H/C and low O/C atomic ratios, and a consistent trend in chemical composition was observed for subsurface water, the surface microlayer, and generated SSA. Although the effect of biological processes on the composition of SSA organic matter was clear, in **Paper II** it was shown that during the phytoplankton bloom, the abundance of organic matter in SSA was fairly constant, without any significant influence on their CCN activity or the particle production flux. **Paper III** provided a mechanistic understanding of the enrichment of different cationic surfactants (CSs) in SSA through experiments conducted using a sea spray simulation chamber. It was shown that enrichment of the CSs was primarily driven by the alkyl chain length of the CSs but also affected by the different functional groups in the CSs. The highest enrichment of CSs on SSA was observed for quaternary amines followed by primary and tertiary amines. Interaction with dissolved humic acid was shown to decrease the enrichment of longer-chain amines while the enrichment was increased for shorter-chain ones. When the plunging jet flow rate was increased, enrichment in SSA was shown to increase, especially for lower water concentrations of surface-active compounds. The purpose of **Paper IV** was to improve the understanding of the enrichment behavior of perfluoroalkyl acids (PFAAs), which are strong anionic surfactants. Similar to CSs, it was shown that increasing the plunging jet flow increased the enrichment on SSA, from 43-88% for different PFAAs. The effect of different inorganic salts present in seawater on enrichment was also tested. Compared to chamber experiments prepared with ~35% NaCl water matrix, it was shown that the presence of other seawater ions, namely Ca^{2+} and Mg^{2+}, increased the enrichment of some PFAAs, especially for those with longer perfluoroalkyl chains.

Keywords: *Sea spray, Organic carbon, Dissolved organic matter, Phytoplankton bloom, Cationic surfactants, Perfluorinated alkyl acids, LC-MS, HRMS.*

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