

Aerosol-halogen interaction: Change of aerosol optical properties

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Reactive halogen species, released by sea-salt activation, offer a class of reactants of utmost importance for heterogeneous reactions with organic aerosols. To study the interaction of organic aerosols with these halogen species, secondary organic aerosol (SOA) was produced from α -pinene, catechol and guaiacol (Ofner et al., 2011) in a 700 L glass smog-chamber and in a 3500 L Teflon smog-chamber at defined environmental conditions (with and without simulated sunlight and ozone at various humidities). The well-characterized and aged organic aerosols were exposed to molecular halogens in the presence of UV/VIS irradiation and to halogens released from simulated natural halogen sources to study the halogen-SOA interaction process.

Various spectroscopic methods were used to investigate optical and structural changes of the organic aerosols. Diffuse reflectance UV/VIS spectroscopy was employed to characterize optical properties in the UV/VIS spectral range. Using FTIR spectroscopy both, the aerosol formation and transformation process and, using ATR (Attenuated Total Reflectance) spectroscopy, the appearance of functional and structural elements of the particulate phase were characterized. Using Temperature-Programmed-Pyrolysis Mass-Spectroscopy (TPP-MS) and Ultra-high resolution Fourier-Transform/Mass-Spectroscopy (ICR-FT/MS), degrees of halogenations and single halogenated molecules could be determined.

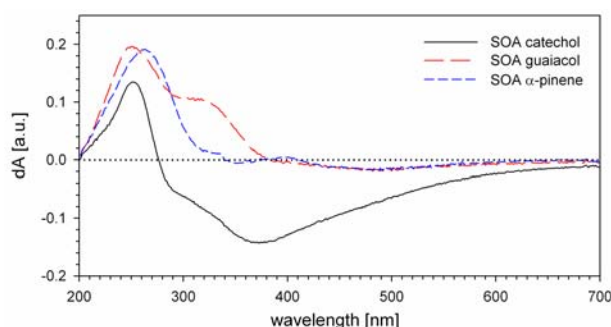


Figure 1. Differential absorbance of the organic aerosols, calculated from the diffuse spectra before and after the reaction with natural released halogens

Overall, the optical properties of organic aerosols appear to be significantly changed due to the reaction with those reactive halogen species. While the interaction with chlorine was found to lead to some bleaching (corresponding to a blue-shift), the reaction with bromine shifts the absorption in the UV/VIS range to the red. Those changes are indicated by calculating the

differential absorbance (dA) from the diffuse UV/VIS spectra (see Fig. 1), where a “bleaching” of the organic aerosols is observed.

Also transformation of relevant functional groups and formation of carbon-halogen bonds was found in the infrared between 800 and 600 cm^{-1} . While the carbonyl stretch region is the most dominant absorption at simulated (from α -pinene, catechol and guaiacol) and natural SOA samples (at about 1730 cm^{-1}), the infrared spectra of the halogenated SOA from the model precursors significantly differ (see Fig. 2) from the reported spectra of unprocessed SOA (Ofner et al., 2011).

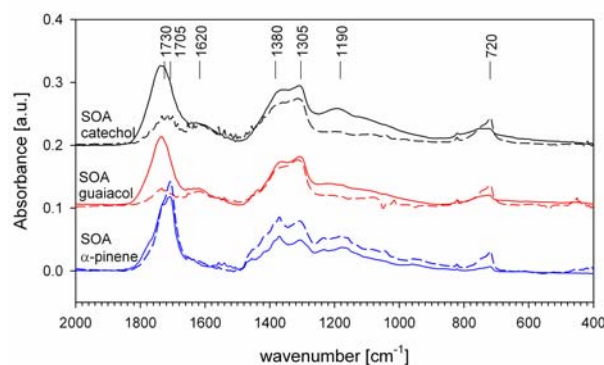


Figure 2. Comparison of ATR FTIR spectra of the unprocessed (solid lines) and halogenated (dashed lines) organic aerosols.

Due to the change of the chemical properties a change of the physical properties is expected, that is related to the atmospheric environment like ability to act as CCN, their potential to adsorb other low-volatile gases or even their contribution to radiative forcing.

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