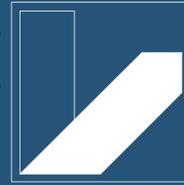


Release of reactive halogen species from sea-salt aerosols and interaction with secondary organic aerosols and HULIS in smog-chamber experiments



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Bayreuth Center of Ecology
and Environmental Research

Natalja Balzer¹, Wolfgang Behnke², Johannes Ofner¹, Frank Siekmann¹, Cornelius Zetzsch^{1,2}

¹ Atmospheric Chemistry Research Laboratory, BayCeer, University of Bayreuth, Germany

² Fraunhofer-Institute of Toxicology and Experimental Medicine, Hannover, Germany

Introduction

Sea-salt aerosol introduces large amounts of fine saline droplets into the lower troposphere. Reactive halogen species can influence the oxidizing capacity of the troposphere, and only the interactions with minerals, sea-salt and ice have been considered so far in the atmospheric aerosol. Besides black carbon and soot there is a fraction of secondary organic aerosol: macromolecules, named HULIS (humic-like substances). These are of interest because they influence aerosol properties, such as light scattering and hygroscopic growth, and may participate in various atmospheric reactions.

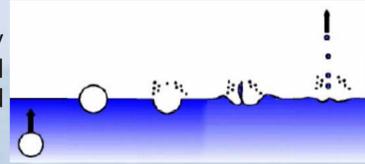
Field experiments and laboratory studies show that atomic Br and Cl are produced from sea-salt aerosol. The halogen release is based on the uptake of gaseous HOX on aqueous, acidified salt surfaces. Br and Cl play an important role in atmospheric ozone depletion and destruction of hydrocarbons. HULIS may take part in these reaction cycles by halogenation and production of volatile and non-volatile organic halogens, and we want to understand their role as inhibitor or catalyst of halogen activation (a reservoir for reactive halogens?) and their flux to ecosystems.

Blue Mountains:
The blue dust is caused
by secondary organic
aerosol (SOA).



Sea salt Activation

Sea-salt aerosol is mainly formed by bubble bursting and is a natural source of atomic chlorine and bromine in the troposphere.



These halogen atoms destroy ozone and form intermediate halogen oxides, regenerating the halogen atoms in cycles from sea salt aerosol. HOBr is transformed in the salt particles to Br₂ or BrCl. After leaving the particle the volatile molecules are photolysed to atomic Br and Cl. Destruction of O₃ forms the halogen oxides BrO and ClO which react with the atmospheric hydroperoxyl radical (HO₂) to form HOBr and HOCl. These are absorbed by the sea-salt aerosol, and the molecular halogens are released again.



This cycle is called "bromine explosion", because a rapid, exponential multiplication of atomic Br occurs, even though chloride concentration in sea salt is much higher. After depletion of aerosol bromide, chlorine is also released as BrCl.

Results



If made of glass, the walls of smog chambers are known to release Cl₂ from ozone and HCl by heterogeneous photochemistry. This artefact is avoided in our chamber, made of Teflon film (3500I, FEP 200A, Dupont), (**Fig. 1**).

Atomising NaCl solutions (1 g/l) with admixed NaBr (up to 15 mg/l) generates aerosol at mass densities of 1 mg/m³. Humidity is kept above deliquescence (>76% r.h.), and residence times of the aerosol range from 3-5 h.

Photochemistry is driven by a solar simulator (HMI lamp, Osram, 1.2 kW), employing [O₃]₀ = 350 - 600 ppb. Information on Br is obtained from observed ozone consumption (**Fig. 2**).

[Cl(t)] and [OH(t)] are determined from the lifetimes of a set of hydrocarbons:

$$\ln \frac{[HC_i]_0}{[HC_i]_t} = k_{OH} [OH(t)]dt + k_{Cl} [Cl(t)]dt$$

The runs deliver final levels of OH-radicals (**Fig. 3**) up to 6x10⁸ cm⁻³. Atomic Cl rises up to 1x10⁶ cm⁻³ (**Fig. 4**). Assuming [HO₂] ~ 40ppt calculations lead to: [BrO] ~ 200 ppt and [ClO] ~ 40 ppt.

Fig. 1: Teflon smog chamber (3500I) can be cooled to -25 °C.

Fig. 2: Ozone depletion, 1 g/l NaCl with various Br-contents

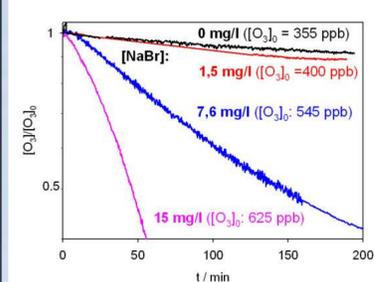


Fig. 3: Integrated formation of OH, the slope delivers the concentration

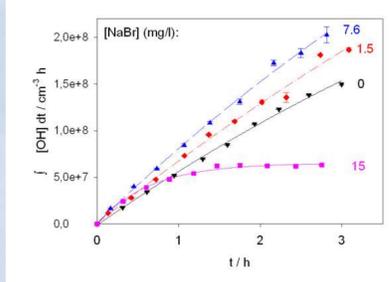
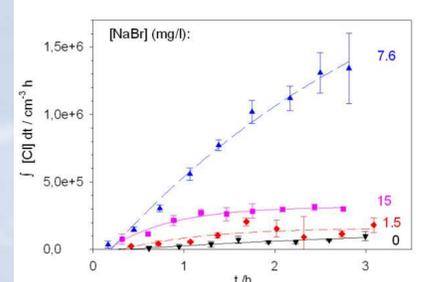


Fig. 4: Integrated formation of Cl, the slope yields the concentration

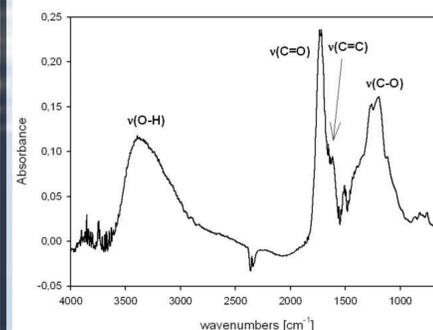


Production of HULIS

Gas-to-particle conversion forms so-called HULIS. These are produced by photochemical reactions of volatile organic compounds. The model compounds catechol and guaiacol are employed in the presence of O₃ and OH under irradiation by a solar simulator (HMI, Osram, 4 kW).



Glass fibre filter coated with HULIS. In fact, the colour of the filter samples resembles to humic substances.



ATR infrared spectrum of secondary organic aerosol containing characteristic group frequencies like C-O, C=C, C=O and O-H.

Experimental techniques

The formation of the secondary organic aerosol and the determination of possible halogenated gaseous and solid organic products are studied using several techniques.

Samples of HULIS are deposited on a ZnSe-ATR-crystal by a home-made electrostatic precipitator and can be analysed using FTIR-spectroscopy.

Analysis of trace gas concentrations is performed by GC-ECD, GC-FID and GC-MS techniques. Long-path FTIR-spectroscopy can be employed for direct spectroscopic investigation of the aerosol in the smog chamber.



700-L smog chamber with FTIR long-path White cell

Acknowledgements

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