CASOMIO

C ondensational Growth
A nd
S urface Reactivity
O f
M ixed
I norganic/
O rganic Aerosols

EC-Programme: Environment, Energy and Sustainable Development

Principal Investigator:

Forschungszentrum Jülich	Thomas F. Mentel
Energy Research Centre of the Netherlands	Harry M. ten Brink
University of Cambridge	R. Anthony Cox
University of Helsinki	Markku Kulmala

Introduction

The fine particle mode of the tropospheric aerosol is important in tropospheric radiative forcing and atmospheric chemistry: the particles scatter sunlight, provide condensation nuclei for cloud droplets, and participate in heterogeneous chemical reactions.

Tropospheric aerosol exerts a cooling effect that possibly counteracts the global warming. However, the degree of compensation is highly uncertain. To become climatically active aerosol must grow to 50 nm (cloud condensation nuclei), or to 100 nm (direct scattering), respectively. In order to determine the climatic importance of atmospheric aerosols, we need to know what are the vapors causing the particle growth, what are the chemical mechanisms controlling their formation, and what if any is the anthropogenic influence on their concentrations.

In fine aerosols particles the organic fraction is usually the second most abundant after sulfates. While the chemistry and the thermodynamics of the inorganic components (aqueous electrolytes) are relatively well understood, by far not enough is known about the organic components. This is partly due to the much greater number of individual organic species involved. Field studies indicate that dissolution of oxidized hydrocarbons into the particulate phase or the formation of organic coatings possibly modify the reactivity of aerosols, constitute transport barriers for gas-liquid mass transfer, and prevent the establishment of Henry equilibria. Heterogeneous hydrolysis reactions would be immediately influenced by such reductions of the surface reactivity or water availability. An ideal candidate to probe this is the N2O5 hydrolysis, since it is well characterized for aqueous inorganic aerosols and thus changes induced by organic components are easily detectable.

Objectives

The objective of the CASOMIO project is to demonstrate how the inorganic and organic aerosol component interact in sub-micron aqueous droplets in two respects a) condensational growth and water affinity and b) surface reactivity of the particulate phase:

- Develop and improve analytical tools for quantitative studies of mixed inorganic/organic aerosols in simulation chambers and field measurements.
- Study the role of organic aerosol components for the surface reactivity of aqueous aerosols, with focus on hydrophobic coatings.
- Study the influence of organic coatings on the heterogeneous NOx removal from the troposphere. This will include the determination of
    - reaction probabilities for N2O5 as function of the organic component in deliquescent and metastable sulfate and nitrate aerosols
    - distribution coefficients of HNO3 as function of the organic component in deliquescent and metastable sulfate aerosols
    - distribution coefficients of organics in ammonium sulfate and nitrate aerosols as a function of the relative humidity, i.e. as function of the ionic strength and the water activity
- Quantitatively understand the role of organic compounds for the thermodynamic properties of mixed inorganic/organic aerosols: the partitioning of organic vapors in ammonium salt aerosols as a function of the relative humidity, the effect of dissolved organics on the liquid water content of the ammonium salt aerosols, and the effect of surface coating by organic detergents
- Quantify the role of organic vapors for particle formation and particle growth

Concept

The concept of CASOMIO is to integrate two experimental techniques with different time and spatial scales and modeling activities on several levels in order to achieve widest applicability of the particular results with respect to the atmosphere:

1. **Flow Tube Experiments:** short contact times between gas-phase molecules and the particulate phase
2. **Large Aerosol Chamber Experiments:** stagnant or slowly varying conditions.
3. **Modeling Activity:** serves to directly realize the role of organic vapors for formation, growth, and hygroscopic properties of secondary aerosols in the troposphere and the implications for the atmospheric chemistry and climate.
    a. *Thermodynamic modeling* to obtain thermodynamically consistent vapor pressures, chemical activities, surface tensions and densities for organic compounds and their water solutions as a function of temperature and composition
    b. *Detailed theoretical modeling* to obtain the growth from 1 nm to 20 nm
    c. *Aerosol dynamic modeling* (nucleation, condensation, coagulation, deposition) with gas phase chemistry to obtain the atmospheric significance of condensation of organic vapors

The CASOMIO project will focus on ammonium sulfate/bisulfate and ammonium nitrate as inorganic aerosol substrates. The organic components will be chosen from known oxidation products of biogenic and anthropogenic hydrocarbons (terpenes and aromatics). Criteria will be the atmospheric importance, i.e. abundance, reactivity or photoactivity. It is planned to investigate typical cases observed or suggested to occur in the atmosphere: high water solubility - high vapor pressure (short chain alcohols and aldehydes), high water solubility - low vapor pressure (short chain acids, bifunctional acids), surface coating (long chain acids). Overall the CASOMIO project will focus on the situations observed for the continental atmosphere.