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Carbonaceous aerosol components: chemical composition, reactitvity, and hygroscopicity (CARBAERO)

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Introduction and Motivation

The effects of aerosols on atmospheric chemistry and physics, climate, and public health are among the central topics in current environmental research. Aerosol particles can scatter or absorb radiation, influence the formation of clouds and precipitation, and affect the abundance of trace gases via heterogeneous chemical reactions and other multiphase processes. Moreover, they can cause respiratory, cardiovascular, and allergic diseases. The primary parameters which determine these effects are particle size, structure, and composition. The concentration and size distribution of aerosol particles in the troposphere is temporally and spatially highly variable, and their physicochemical properties and transformation (aging) are poorly understood.

In the lower troposphere carbonaceous aerosol components (organics and elemental carbon) account for up to ˜ 50 % of fine air particulate matter. The total carbon content (TC) is usually determined by thermochemical analysis and divided into an elemental carbon (EC) or black carbon (BC) fraction and an organic carbon fraction (OC). There is, however, a more or less gradual decrease of thermochemical refractiveness and specific optical absorption going from graphite-like structures to non-refractive and colorless organic compounds. Depending on the applied thermochemical and optical methods, EC and BC measurements include not only graphite-like material from soot and other combustion particles but also refractory or colored organics. This can lead to substantially different results and limits the comparability and suitability of BC, EC, and OC data for the determination of mass balances and physicochemical properties of air particulate matter (“How black is black carbon?”). Besides differ-

ent types of graphite-like materials there are at least two classes of organics which can contribute to the absorption of visible light by air particulate matter: polycyclic aromatics and humic-like substances. Hundreds of organic compounds have been determined but only 10-40 % of the total organic particulate matter (OPM) in air have been identified at a molecular level. Most organics can efficiently interact with atmospheric photooxidants and water, but the mechanisms and rate parameters of mass transport and chemical reactions are hardly known (Ammann et al., 2003; Ammann and Pöschl, 2005; Pöschl, 2002; 2003; and references therein). Therefore the project CARBAERO was aimed at the experimental investigation and mechanistic description of the chemical composition, reactive transformation, and water interaction of carbonaceous aerosol components. The investigations were focused on biopolymers, humic-like substances, polycyclic aromatic compounds, and elemental carbon.

Methods and Results

Within the project CARBAERO research activities have been pursued and scientific results have been achieved in the following areas:

1) Development and optimisation of analytical methods (liquid and solid phase extraction, liquid and gas chromatography, optical spectroscopy and mass spectrometry, enzymatic and immunochemical assays, etc.) for the determination of carbonaceous aerosol components: polycyclic aromatic hydrocarbons (PAH, Bömmel et al., 2003; Schauer et al., 2003); nitrated and oxygenated PAH derivatives (Letzel et al., 2001; Schauer et al., 2004); proteins and nitrated derivatives (Franze et al., 2003a; 2004; Walcher et al., 2003); elemental carbon (Sadezky et al., 2004); cellulose, humic-like substances, and water-soluble organic carbon (Schaller et al., 2003).

2) Aerosol field measurements at urban, rural, and high-alpine locations (Munich, Hohenpeissenberg, Schneefernerhaus/Zugspitze; measurement of particle number concentrations and size distributions; gravimetric and chemical analysis of filter and impactor samples; determination of PM2.5, TC, EC, PAH, nitro-PAH, proteins): detection of high protein concentrations (up to 7 % of PM2.5; Franze et al., 2003b); characterisation of PAH filter sampling artefacts (up to 100 %; linear correlation with ambient ozone; Schauer et al., 2003); detection of nitro-PAH in a high alpine clean air environment (Schauer et al., 2004); observation of characteristic local differences and seasonal trends of aerosol physical properties and chemical composition (Franze et al., 2003b; Schauer et al., 2003; 2004; Zerrath et al., 2003).

3) Experimental investigation and mathematical modelling of the interaction of aerosol particles and components (soot/PAH, proteins) with reactive trace gases (O3, NO2) and water vapor: identification of previously unknown PAH nitration and oxidation products (Schauer et al., 2004); detection of efficient protein nitration by polluted

air and synthetic gas mixtures (Franze et al., 2003a; Franze et al., 2005); deconvolution of adsorption and surface reaction processes and determination of adsorption equilibrium and reaction rate parameters for O3, NO2, and H2O on soot/PAH (Pöschl et al., 2001; Pöschl, 2002); development of a kinetic model framework for aerosol surface reactions and gas-particle interactions (Ammann et al., 2003; Ammann and Pöschl, 2005; Pöschl et al., 2005).

4) Experimental investigation and mathematical modelling of the interaction of water vapor with aerosol particles of complex chemical composition (mixtures of salts and biopolymers, etc.): electric charge effects and microstructural rearrangements; phase transitions and hygroscopic growth; kinetic limitation of deliquescence and water uptake by protein envelopes; parameterisation of the practical osmotic coefficient for globular macromolecules (Mikhailov et al., 2004).

Summary and Conclusions

The abundance and molecular structures of carbonaceous aerosol components and their interaction with water and reactive trace gases have been investigated in laboratory experiments, field measurements and model calculations. New and improved analytical techniques and model formalisms have been developed and applied. Some of the scientific results and implications have already been presented and discussed in journal articles (see references), and several further publications are in preparation. While some of the investigations are still under way, the most innovative findings and conclusions achieved up to now can be summarized as follows:

1) Determination of high concentrations of biopolymers and biological particles in the fine fraction of atmospheric aerosols, which may efficiently influence cloud condensation and ice nucleation (electric and kinetic effects) and indicate that the biosphere acts as a major source not only for secondary but also for primary organic particles.

2) Discovery of efficient protein nitration by polluted air (nitrogen oxides and ozone), which may influence the chemical, optical, and microphysical properties and effects of biological particles in the atmosphere and provides a molecular rationale for the promotion of allergies by traffic related air pollution.

3) Mechanistic elucidation and quantitative description of the interaction of photooxidants with polycyclic aromatic compounds and soot particle surfaces (reversible and competitive adsorption followed by irreversible surface reaction), which implies rapid chemical aging of combustion particles in the atmosphere and upon sampling with traditional techniques (artefacts up to 100 %).

4) Development of a kinetic model framework with consistent and universally applicable terminology and rate equations for gas-particle interactions in aerosols and

clouds (transport/reaction, liquid/solid, surface/bulk, reversible/irreversible, competitive/consecutive).

References and Acknowledgement

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