Aging Processes of Soot Particles in the Atmosphere

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Soot particles are emitted by all kinds of incomplete combustion processes and consist of a mixture of elemental and organic carbon (EC and OC). Besides the soot mode at a particle diameter of about 100 nm a second mode is clearly seen in traffic-influenced areas, with a diameter around 20 to 30 nm (Weingartner et al., 1997a, Bukowiecki et al., 2002). These particles are formed by condensation of semivolatile exhaust components and therefore disappear to a large extent in a thermal desorber (Baltensperger et al., 2002). Coagulation results in a rapid decrease of the number concentration of these condensation particles (typically 1 hour, Bukowiecki et al., 2002), while the soot particles have much longer lifetimes. Atmospheric aging processes result in a significant change of the chemistry of these soot particles.

The hygroscopic properties of aerosols play a crucial role in climate impact, air quality, acid deposition, biochemical cycles, visibility reduction, and the formation of clouds and precipitation. Hygroscopicity measurements are a suitable means to detect the degree of this chemical transformation, since most of these aging processes lead to an enhanced water solubility of the particles. At high relative humidity (RH) water is often the dominant component of the ambient aerosol. If an aerosol particle is transferred from low to high RH, its diameter may change by up to a factor of 3. This ability to absorb water strongly depends on the particle “dry” size, shape and chemical composition, and hence the age.

The response of aerosol particles on changes in RH are commonly measured by means of a so-called Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) (Weingartner et al., 2002). This instrument is suited for a nearly artefact free measurement of the hygroscopic growth factor D/De defined as the ratio of the humidified diameter D to the dry diameter De. The H-TDMA was operated during different extensive field campaigns conducted during different seasons at the high alpine site Jungfraujoch. During most of the time, the station was located in the free troposphere, and the shape of the humidified H-TDMA size spectra were preferentially characterized by a narrow monomodal growth distribution (see Figure 1). This implies that the particles in the observed size range were to a large extent internally mixed, as regards their hygroscopic and chemical properties. This is in contrast to the behavior of continental polluted aerosols where the particles generally separate into a less- and more-hygroscopic group, i.e. an external mixture of freshly emitted combustion particles (less hygroscopic) and a background aerosol (more hygroscopic). It can also be seen that the hygroscopic modes at the Jungfraujoch have a significantly higher hygroscopicity than the modes at Milano, indicating that atmospheric aging processes lead to a substantial increase in particle hygroscopicity.

Figure 1: Typical examples of measured hygroscopic growth distribution at RH = 85% in Milan and at the Jungfraujoch showing that the free tropospheric aerosol particles experience a significantly higher hygroscopicity than the aerosol at an urban site. The dotted line is the distribution of the originally dry, monodisperse aerosol particles with a modal diameter of De = 100 nm (data from Weingartner et al., 2002 and Baltensperger et al., 2002).
Directly after their emission, soot particles are hydrophobic, i.e., both EC and OC are water insoluble, and the particles grow only little upon exposure to high RH (Weingartner et al., 1997b). After aging, i.e., at a remote site such as the Jungfraujoch, the carbonaceous material is internally mixed with a high fraction of water soluble material (typically 80 to 90%), which results in a monomodal distribution of the growth factor. Typically 50% of the organic carbon of this aged aerosol is water soluble (Krivacsy et al., 2001).

Processes that contribute to this increased growth factor are: (1) coagulation with water soluble particles, (2) (photo)-chemical degradation of the aerosol particle surface, (3) gas to particle conversion (heterogeneous nucleation), (4) adsorption and reaction of gaseous molecules and (5) cloud processing.

Coagulation is not very efficient in changing the chemical characteristics of the soot particles. Much more efficient is the condensation of condensable molecules such as secondary organic aerosol produced by photochemical oxidation of gaseous precursors (Saathoff et al., 2002). This condensation significantly changes also the optical properties of the soot particles, since a layer of scattering material greatly enhances the absorption efficiency of the soot (Schnaiter et al., 2002). Absorption and reaction of gaseous molecules may also result in significant changes of the chemistry of the soot particles, even though this process is usually limited to the surface of the particles. This is exemplified by the reaction of NO2 and diesel soot (Gutzwiller et al., 2002 and references therein). (Photo)-chemical degradation may be exemplified by the rapid decrease of polycyclic aromatic hydrocarbons on the surface of soot particles by reaction with NO2 or OH, or with ozone (Pöschl et al., 2001). Finally, cloud processes are also an efficient process in adding water soluble material to the aerosol particles, e.g. by SO2 oxidation in the cloud droplets (Weingartner et al. 1999). However, for this process the particles require a certain size to be activated during cloud formation (Henning et al., 2002).

References

Atmospheric aging processes of soot particles

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Freshly emitted soot particles  Background aerosol

Which transformation processes change the particles physical and chemical properties?

Close to the source

High-alpine research station Jungfraujoch
3580 m asl
Motivation

• The global emissions of carbonaceous particles from anthropogenic sources (BC) are estimated at 11–17 Tg/y (~50% biomass burning, 50% fossil fuel) (www.ipcc.ch)

• The size distribution of soot particles peaks in the accumulation size range, therefore dry deposition velocities are small and soot particles can attain long lifetimes and be transported over long distances. They are mainly removed by wet deposition.

• Soot particles are an important constituent of the atmospheric aerosol, since they affect human health and scatter and absorb light
Radiative Forcing by Tropospheric Aerosols

**Direct Effect**

Scattering and Absorption of incoming sunlight by aerosol particles.

**Indirect Effect**

The number of CCNs influences the cloud droplet size and thereby changes the cloud albedo and lifetime.
The global mean radiative forcing of greenhouse gases and aerosols for the year 2000, relative to 1750

Source: www.ipcc.ch
Indirect effect of carbonaceous particles:
Ship tracks

Ship tracks on the East Atlantic

Aerosol particles emitted by ships (soot particles with a high sulfur content) act as CCN and form clouds and enhance cloud reflectivity.
Aging processes of soot particles in the atmosphere

*(Photo)-chemical degradation of the aerosol particle surface*

Gas to particle conversion (heterogeneous condensation)

Coagulation with (dry) water soluble particles, e.g. \((\text{NH}_4)_2\text{SO}_4\)

Liquid phase reactions, immersion in solution droplets

- Fractal-like dimension, \(d_f\)
- Hygroscopicity, \(D/D_0 @ \text{RH} = 85\%\)
- Light absorption efficiency

- \(~2\)
- \(~1.01\)
- \(~3\)
- \(> 1.4\)

2-4 times higher
Hygroscopic Growth Factor of Aerosol Particles in Milano and at the Jungfraujoch

- dry
- Milan Summer 1998
- JFJ Summer 2002
- JFJ Winter 2001
- JFJ Winter 2004

RH = 85%

$D_o = 100$ nm
Aerosol volume experience a lower volatility close to the sources

Volatilization temperatures:

$\text{H}_2\text{SO}_4$ : ~90°C

Organics: 20 - ~400°C

$(\text{NH}_4)_2\text{SO}_4 / \text{NH}_4\text{HSO}_4$: 150°C

Soot: >300°C

NaCl, Mineral dust: > 600°C

Chemical composition of the Jungfraujoch aerosol during summer

Analyzed offline with IC, solid phase extraction combined with TOC Analyzer
Summer 1998, PM2.5, 8 High Vol Samples

Krivácsy et al. (2001)
J. Atmos. Chem, 39, p235
Absorption

What is the effect of coating on the absorption of carbonaceous particles?
The mixing state is important!

**External Mixture**
BC particles are separated from scattering particles

**Coated Internal Mixture**
BC particles are coated with a scattering material

**Homogeneous Internal Mixture**
BC is mixed with scattering components throughout the particle
Enhancement of the absorption coefficient by coating Diesel soot particles with scattering material

In collaboration with the AIDA crew, Forschungszentrum Karlsruhe
Encapsulating carbonaceous particles with scattering material results in enhanced absorption

Ammonium sulfate: $n = 1.53 + 0.00\ i$

Coating with ammonium sulfate: up to a 4 times higher absorption for the mixed particle!

Model calculation with Lorenz-Mie theory
Fuller et al. JGR (1999)
Model calculation for the conditions at the Jungfraujoch (polydisperse size distribution and coating including the hygroscopic properties)

Enhancement in absorption

Relative coating thickness

R. Nessler et al., Submitted to JAS 2004

Insoluble, light absorbing core

+ water soluble coating mix of organic and inorganic substances

dry particle + rel. humidity

Ambient aerosol (solution droplet)
Reasons for the uncertainties in the estimation of the radiative forcing of BC:
different assumption about the mixing state and lack of a precise BC emission inventory
Conclusions

• Aging processes affect the hygroscopic behavior, the optical properties and the lifetime of the soot particles

• The mixing state of carbonaceous aerosol is important in determining its radiative effect.

• While freshly emitted soot particles are initially hydrophobic and externally mixed, they are transferred into an internal mixture by coagulation, condensation or photochemical processes.
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Method for measuring scavenged fraction in clouds

Scavenging Ratio = \( \frac{N_{\text{cloud}}}{N_{\text{total}}} = \frac{N_{\text{TOT}} - N_{\text{INT}}}{N_{\text{TOT}}} \)
Correlation of Scavenged BC and (SMPS-)Volume in Summer (CLACE 2)

In Summer, on average, 48% of the total BC concentration is present in the cloud phase (i.e. is activated to cloud droplets)

Winter data (CLACE3) is different!
Winter data: The fraction of activated BC decreases with temperature.

-> BC activation in mixed phase clouds is different!