

Atmospheric Aerosols: Composition, Transformation, Climate and Health Effects

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Aerosols are of central importance for atmospheric chemistry and physics, the biosphere, climate, and public health. The airborne solid and liquid particles in the nanometer to micrometer size range influence the energy balance of the Earth, the hydrological cycle, atmospheric circulation, and the abundance of greenhouse and reactive trace gases. Moreover, they play important roles in the reproduction of biological organisms and can cause or enhance diseases. The primary parameters that determine the environmental and health effects of aerosol particles are their concentration, size, structure, and chemical composition. These parameters, however, are spatially and temporally highly variable. The quantification and identification of biological particles and carbonaceous components of fine particulate matter in the air (organic compounds and black or elemental carbon, respectively) represent demanding analytical challenges. This Review outlines the current state of knowledge, major open questions, and research perspectives on the properties and interactions of atmospheric aerosols and their effects on climate and human health.

From the Contents

1. Introduction	7521
2. Composition and Analysis	7523
3. Chemical Reactivity and Water Interactions	7527
4. Climate and Health Effects	7532
5. Summary and Outlook	7535
6. Appendix	7536

1. Introduction

The effects of aerosols on the atmosphere, climate, and public health are among the central topics in current environmental research. Aerosol particles scatter and absorb solar and terrestrial radiation, they are involved in the formation of clouds and precipitation as cloud condensation and ice nuclei, and they affect the abundance and distribution of atmospheric trace gases by heterogeneous chemical reactions and other multiphase processes.^[1–4] Moreover, airborne particles play an important role in the spreading of biological organisms, reproductive materials, and pathogens (pollen, bacteria, spores, viruses, etc.), and they can cause or enhance respiratory, cardiovascular, infectious, and allergic diseases.^[1,5–7]

An aerosol is generally defined as a suspension of liquid or solid particles in a gas, with particle diameters in the range of 10^{-9} – 10^{-4} m (lower limit: molecules and molecular clusters; upper limit: rapid sedimentation).^[4,7] The most evident examples of aerosols in the atmosphere are clouds, which consist primarily of condensed water with particle diameters on the order of approximately 10 μ m. In atmospheric science, however, the term aerosol traditionally refers to suspended particles that contain a large proportion of condensed matter other than water, whereas clouds are considered as separate phenomena.^[8]

Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. Primary particles are directly emitted as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven or traffic-related suspension of road, soil, and mineral dust, sea salt, and biological materials (plant fragments, microorganisms, pollen, etc.). Secondary particles, on the other hand, are formed by gas-to-particle conversion in the atmosphere (new particle formation by nucleation and condensation of gaseous pre-

cursors). As illustrated in Figure 1, airborne particles undergo various physical and chemical interactions and transformations (atmospheric aging), that is, changes of particle size, structure, and composition (coagulation, restructuring, gas uptake, chemical reaction). Particularly efficient particle aging occurs in clouds, which are formed by condensation of water vapor on preexisting aerosol particles (cloud condensation and ice nuclei, CCN and IN^[+]). Most clouds reevaporate, and modified aerosol particles are again released from

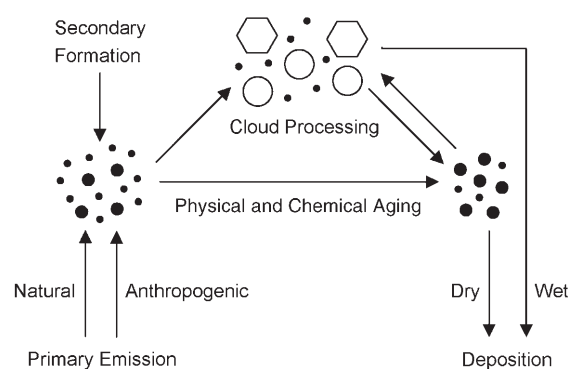


Figure 1. Atmospheric cycling of aerosols.

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[‡] A list of abbreviations can be found at the end of the Review.

the evaporating cloud droplets or ice crystals (cloud processing). If, however, the cloud particles form precipitation which reaches the Earth's surface, not only the condensation nuclei but also other aerosol particles are scavenged on the way to the surface and removed from the atmosphere. This process, termed "wet deposition", is actually the main sink of atmospheric aerosol particles. Particle deposition without precipitation of hydrometeors (airborne water particles)—that is, "dry deposition" by convective transport, diffusion, and adhesion to the Earth's surface—is less important on a global scale, but is highly relevant with respect to local air quality, health effects (inhalation and deposition in the human respiratory tract), and the soiling of buildings and cultural monuments. Depending on aerosol properties and meteorological conditions, the characteristic residence times (life-times) of aerosol particles in the atmosphere range from hours to weeks.^[9,10]

The concentration, composition, and size distribution of atmospheric aerosol particles are temporally and spatially highly variable. In the lower atmosphere (troposphere) the total particle number and mass concentrations typically vary in the range of about 10^2 – 10^5 cm^{-3} and 1 – 100 $\mu\text{g m}^{-3}$, respectively.^[9–12] In general, the predominant chemical components of air particulate matter (PM) are sulfate, nitrate, ammonium, sea salt, mineral dust, organic compounds, and black or elemental carbon, each of which typically contribute about 10–30% of the overall mass load. At different locations, times, meteorological conditions, and particle size fractions, however, the relative abundance of different chemical components can vary by an order of magnitude or more.^[1,4,9,13] In atmospheric research the term "fine air particulate matter" is usually restricted to particles with aerodynamic diameters ≤ 1 μm (PM₁) or ≤ 2.5 μm (PM_{2.5}). In air pollution control it sometimes also includes larger particles up to 10 μm (PM₁₀).

Characteristic examples of particle number concentration, size distribution, and chemical composition of fine particulate matter in urban and high alpine air are illustrated in Figure 2. The displayed particle number size distributions (particle number concentration per logarithmic decade of particle diameter, $\text{d}N/\text{d}(\log d_p)$) plotted against particle diameter) were observed in the city of Munich (500 m above sea level; December 8–14, 2002) and at the Schneefernerhaus research station on Mount Zugspitze (2600 m above sea level;

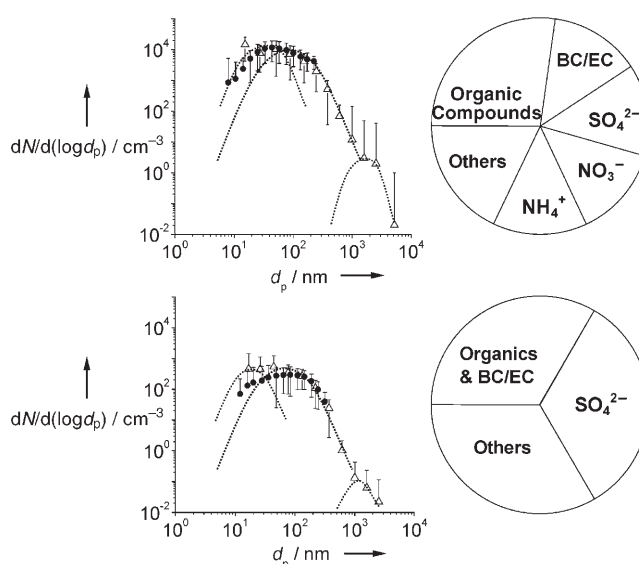
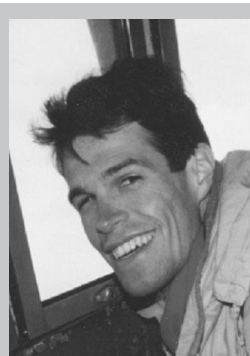


Figure 2. Characteristic examples of aerosol particle-size distribution and chemical composition in urban (top) and high alpine air (bottom). Graphs (left): number size distribution function $\text{d}N/\text{d}(\log d_p)$ (symbols and error bars: arithmetic mean values and standard deviations, Δ ELPI, \bullet SMPS, characteristic particle size modes). Pie charts (right): typical mass proportions of main components.

November 6, 2002) in Southern Germany. They correspond to total particle number concentrations of about 10^2 cm^{-3} in alpine air and 10^4 cm^{-3} in urban air, and to particle mass concentrations of about 1 $\mu\text{g m}^{-3}$ and 10 $\mu\text{g m}^{-3}$, respectively. The measurements were performed with a couple of complementary techniques, an electrical low-pressure impactor (ELPI, 10 nm– 10 μm , flow rate 30 L min^{-1} , measurement interval 1 min) and a scanning mobility particle sizer (SMPS, 10 – 300 nm, flow rate 1 L min^{-1} , measurement interval 30 min).^[14,15] The deviations at very low particle size can be attributed to wall losses by diffusion in the SMPS system. The dotted lines indicate characteristic particle size modes, which can be attributed to different sources, sinks, and aging processes of atmospheric particles: nucleation (Aitken), accumulation, and coarse modes.^[4,7] In corresponding mass size distributions, which are obtained by multiplication with particle volume ($d_p^3 \pi/6$) and density (typically around 2 g cm^{-3}), the nucleation mode is usually negligible whereas accommodation and coarse particle modes are of comparable magnitude. The composition pie charts are based on chemical analyses of PM_{2.5} filter samples from the same locations and literature data for urban and remote continental background air.^[1,4,9,13,16–19]

Figure 3 illustrates the interdependence of composition, composition-dependent properties, atmospheric interactions and transformation, climate and health effects, and aerosol sources. The resulting feedback loops are of central importance in the science and policy of environmental pollution and global change. Thus a comprehensive characterization (climatology) and mechanistic understanding of particle sources, properties, and transformation is required for the quantitative assessment, reliable prediction, and efficient control of



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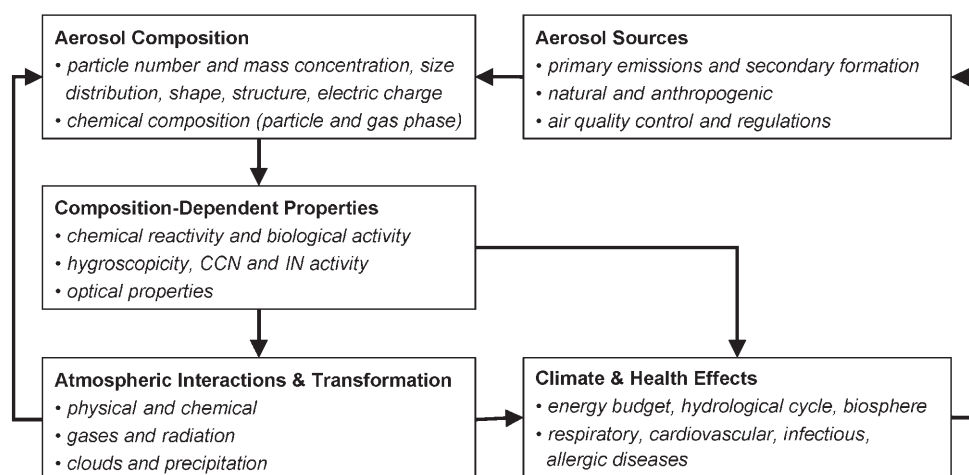


Figure 3. Interdependence and feedback between atmospheric aerosol composition, properties, interactions and transformation, climate and health effects, and sources.

natural and anthropogenic aerosol effects on climate and public health.

2. Composition and Analysis

A wide range of methods can be and have been applied for the physical and chemical analysis of aerosol particles and components.^[1,20–22] Major analytical procedures and measurement techniques are outlined in Figure 4. In practice, the selection and combination of analytical methods depend on the sample type and target parameters (single particles or particle ensembles, suspended or deposited particles, physical properties or chemical composition, etc.) and requires a trade-off between sensitivity and selectivity, time and size resolution, and equipment and labor expenses.

The techniques most frequently applied for the physical characterization of atmospheric aerosol particles are: differential mobility analysis (DMA), inertial separation (impaction, time-of-flight), scanning and transmission electron microscopy (SEM, TEM), and light scattering (Mie) for particle size, structure, and density; β -ray attenuation, gravimetry, and oscillation of deposition substrates for particulate mass; spectrophotometry, photoacoustic spectroscopy, and nephelometry for absorption and scattering coefficients. Some advanced methods for the determination of physical and chemical aerosol properties involve multiple iterative steps of particle conditioning and sizing as indicated by the arrows in Figure 4. Examples are volatility and hygroscopicity tandem differential mobility analysis (V- and H-TDMA) or the online coupling of particle sizing, vaporization, and mass spectrometry with electron-impact (EI) or laser-desorption ionization (LDI). Detailed descriptions and explanations of these and related techniques can be found in recent monographs, reviews, and research articles.^[1,20,22–28]

Accurate determination of the chemical composition of air particulate matter is a formidable analytical task. Minute sample amounts are usually composed of several main constituents and hundreds of minor and trace constituents. Moreover, the composition of the individual particles can be

fairly uniform (internally mixed aerosols) or very different from the ensemble composition (externally mixed aerosols), depending on the particle sources and atmospheric aging processes involved (coagulation, gas-particle partitioning, chemical reactions). Especially in populated environments, air particulate matter can be pictured as the result of an “exploded pharmacy”, comprising just about any non- or semivolatile chemical compound occurring in the biosphere, hydrosphere, and lithosphere, or released by

human activity. Besides primary chemical components, which are directly emitted by natural and anthropogenic sources, air particulate matter mostly also contains secondary chemical components, which are formed by gas-phase reactions and subsequent gas-to-particle conversion or by chemical transformation of primary particle components in the atmosphere.

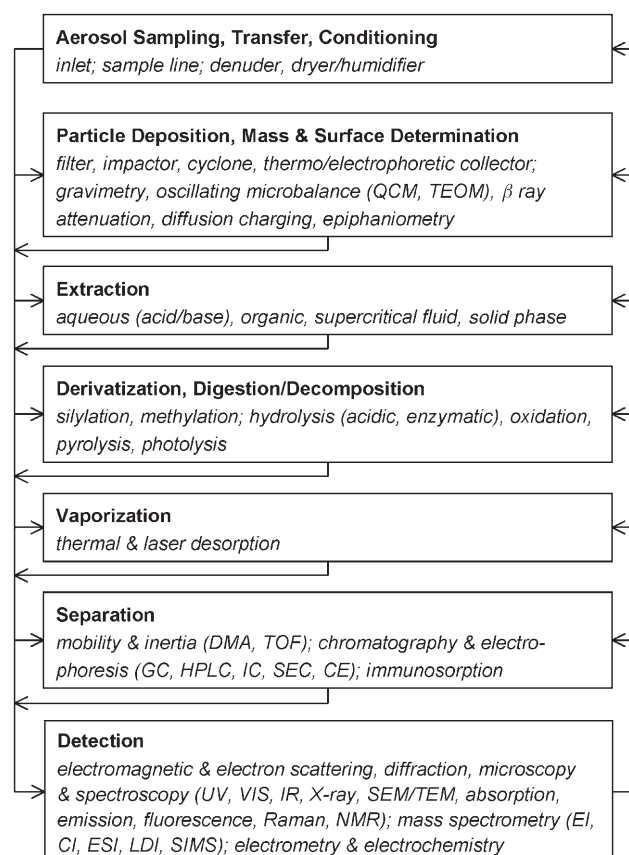


Figure 4. Major analytical procedures and techniques for the physical and chemical characterization of aerosol particles and components: arrows illustrate flexible combination and iterative application of individual steps and methods; acronyms are defined in the appendix.

By definition, an aerosol is composed of particulate and gas-phase components, that is, the term aerosol component can refer to chemical compounds in condensed as well as in the gaseous state. In practice and in the remainder of this manuscript, however, the term aerosol component usually refers to semi- and nonvolatile particle components but not to volatile compounds residing almost exclusively in the gas phase.

Most traditional methods for the sampling and chemical analysis of air particulate matter are “offline” and involve the collection of the investigated particles on solid deposition substrates (membrane or fiber filters, inertial impaction plates, thermal or electrostatic precipitation plates) or in a liquid (wetted wall cyclone, impinger, or washing bottle) and intermediate steps of sample storage, transport, and preparation before chemical analysis.^[1,20,22] These methods are prone to analytical artifacts caused by evaporation of particle components, adsorption or absorption of additional gas-phase components, and chemical reaction during sample collection, storage, transport, and preparation. The potential for measurement artifacts is particularly high for reactive and semivolatile organic aerosol components, and elaborate sampling techniques combining parallel or consecutive trains of denuders, filters, and adsorbent cartridges have been developed to minimize or at least quantify the effects outlined above.^[1,19,20,29,30]

Besides the problem of sampling artifacts, offline techniques hardly allow the resolution of the high spatial and temporal variability of atmospheric aerosols. Over the past few years, however, substantial progress has been made in the development of aerosol mass spectrometers for real-time measurements of size-selected (single) particles. As the methods of vaporization, ionization, calibration, and data analysis are improved, these instruments promise reliable quantitative analyses, especially for chemical elements and inorganic species. Some of them also allow differentiation between surface and bulk composition, but the influence of matrix effects on vaporization and ionization efficiencies and thus on the interpretation of the measurement data still remains to be sorted out reliably. Advances in this rapidly moving field have been reported in a growing number of research and review articles.^[20,25–28,31–40]

A particularly challenging application of aerosol mass spectrometry with high relevance for public health and security is the identification of biological particles and pathogens (bacteria, viruses, spores, etc.).^[25,41,42] Alternative concepts for online monitoring of bioaerosols are based on aerodynamic sizing and fluorescence spectroscopy,^[43] whereas most other applicable techniques are offline and highly labor intensive (cultivation, staining, fluorescence and electron microscopy, enzyme and immunoassays, DNA analysis, etc.).^[18,44–52]

2.1. Carbonaceous Aerosol Components

Carbonaceous aerosol components (organic compounds and black or elemental carbon) account for a large fraction of air particulate matter, exhibit a wide range of molecular

structures, and have a strong influence on the physicochemical, biological, climate- and health-related properties, and effects of atmospheric aerosols.^[1,4,19,53–56]

Traditionally the total carbon (TC) content of air particulate matter is defined as the sum of all carbon contained in the particles, except in the form of inorganic carbonates. TC is usually determined by thermochemical oxidation and evolved gas analysis (CO₂ detection), and divided into an organic carbon (OC) fraction and a black carbon (BC) or elemental carbon (EC) fraction. Measurements of BC and EC are generally based on optical and thermochemical techniques, and OC is operationally defined as the difference between TC and BC or EC (TC = BC + OC or TC = EC + OC).^[19] As illustrated in Figure 5, however, there is no real sharp

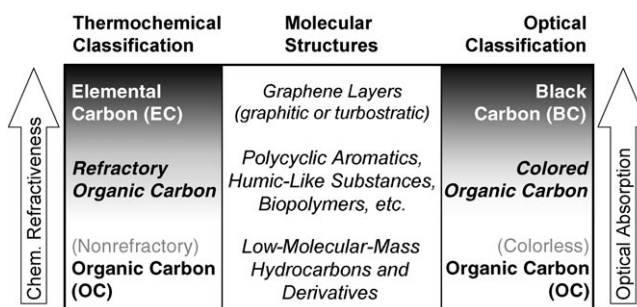


Figure 5. Optical and thermochemical classification and molecular structures of black carbon (BC), elemental carbon (EC), and organic carbon (OC = TC – BC or TC – EC).^[57] Depending on the method of analysis, different amounts of carbon from refractory and colored organic compounds are included in OC and BC or EC.

boundary but a continuous decrease of thermochemical refractivity and specific optical absorption going from graphite-like structures to nonrefractive and colorless organic compounds, respectively.^[57] Both BC and EC consist of the carbon content of the graphite-like material usually contained in soot (technically defined as the black product of incomplete hydrocarbon combustion or pyrolysis) and other combustion aerosol particles, which can be pictured as more or less disordered stacks of graphene layers or large polycyclic aromatics.^[58,59] Depending on the applied optical or thermochemical methods (absorption wavelength, temperature gradient, etc.), however, BC and EC measurements also include the carbon content of colored and refractory organic compounds, which can lead to substantially different results and strongly limits the comparability and suitability of BC, EC, and OC data for the determination of mass balances and physicochemical properties of air particulate matter.

Nevertheless, most information available on the abundance, properties, and effects of carbonaceous aerosol components so far is based on measurement data of TC, OC, and BC or EC.^[19,56] These data are now increasingly complemented by measurements of water-soluble organic carbon (WSOC), its macromolecular fraction (MWSOC), and individual organic compounds as detailed in Section 2.2. Moreover, the combination of thermochemical oxidation with ¹⁴C isotope analysis (radiocarbon determination in evolved

CO₂ by accelerator mass spectrometry) allows a differentiation between fossil-fuel combustion and other sources of carbonaceous aerosol components. Recent results confirm that the EC is dominated by fossil-fuel combustion and indicate highly variable anthropogenic and biogenic sources and proportions of OC.^[60]

Characteristic mass concentrations and concentration ratios of fine air particulate matter (PM_{2.5}) and carbonaceous fractions in urban, rural, and alpine air in central Europe are summarized in Table 1. The reported data have been obtained

Table 1: Characteristic aerosol data for urban, rural, and high alpine air in central Europe.^[a]

	Urban (Munich)	Rural (Hohenpeissenberg)	Alpine (Zugspitze)
PM _{2.5} [$\mu\text{g m}^{-3}$]	20 \pm 10	10 \pm 5	4 \pm 2
TC in PM _{2.5} [%]	40 \pm 20	30 \pm 10	20 \pm 10
EC in TC [%]	50 \pm 20	30 \pm 10	30 \pm 10
OC in TC [%]	40 \pm 20	70 \pm 10	70 \pm 10
WSOC in TC [%]	20 \pm 10	40 \pm 20	60 \pm 20
MWSOC in WSOC [%]	30 \pm 10	50 \pm 20	40 \pm 20

[a] Rounded arithmetic mean values \pm standard deviation determined from about 30 filter samples collected at each location during 2001–2003.

on an altitude transect through Southern Germany, from the city of Munich (500 m above sea level), via the meteorological observatory Hohenpeissenberg (1000 m above sea level), to the environmental research station Schneefernerhaus on Mount Zugspitze (2600 m above sea level) during 2001–2003. The sampling locations and measurement procedures have been described in detail elsewhere,^[61,62] and the results are consistent with those of other studies performed at comparable locations.^[9,11,13,16–19]

On average, the total PM_{2.5} mass concentration decreases by about a factor of 2 from urban to rural and from rural to alpine air, whereas the TC mass fraction decreases from around 40 % to 20 %. The EC/TC ratios in PM_{2.5} are as high as 50 % in the urban air samples taken close to a major traffic junction and on the order of approximately 30 % in rural and high alpine air, demonstrating the strong impact of diesel soot and other fossil-fuel combustion or biomass-burning emissions on the atmospheric aerosol burden and composition. The water-soluble fraction of organic carbon (WSOC in OC), on the other hand, exhibits a pronounced increase from urban (\approx 20 %) to rural (\approx 40 %) and high alpine (\approx 60 %) samples of air particulate matter. This observation can be attributed to different aerosol sources (e.g. water-insoluble combustion particle components versus water-soluble biogenic and secondary organic particle components) but also to chemical aging and oxidative transformation of organic aerosol components, which generally increases the number of functional groups and thus the water solubility of organic molecules (Section 3).

Figure 6 illustrates a characteristic example of the size distribution of TC in air particulate matter sampled at the meteorological observatory Hohenpeissenberg. It exhibits an absolute maximum for particles with aerodynamic diameters on the order of approximately 300 nm, which is likely due to combustion and secondary organic aerosol (SOA) particles

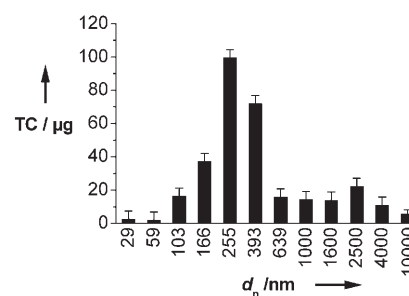


Figure 6. Total carbon content of a size-separated sample of rural air particulate matter plotted against the lower limits of the particle size classes (cut-off diameter of the impaction stages) of the applied electrical low-pressure impactor (ELPI, Hohenpeissenberg, May 27–June 6, 2002; error bars indicate TC measurement uncertainty).

and another local maximum at 2.5 μm , which may be due to primary biological particles or soil dust.

Black or elemental carbon accounts for most of the light absorption by atmospheric aerosols and is therefore of crucial importance for the direct radiative effect of aerosols on climate.^[63–65] Despite a long tradition of soot and aerosol research, however, there is still no universally accepted and applied operational definition of BC and EC. Several studies have compared the different optical and thermal methods applied by atmospheric research groups to measure BC and EC. Depending on techniques and measurement locations, fair agreement has been found in some cases, but mostly the results deviated considerably (up to 100 % and more).^[66–68]

Optical methods for the detection of BC are usually nondestructive and allow (near)-real-time operation, but on the other hand they are particularly prone to misinterpretation. They generally rely on the assumptions that BC is the dominant absorber and exhibits a uniform mass-specific absorption coefficient or cross-section. Although these assumptions may be justified under certain conditions, they are highly questionable in the context of detailed chemical characterization of aerosol particles (“How black is black carbon?”).^[57] Besides different types of graphite-like material, there are at least two classes of organic compounds that can contribute to the absorption of visible light by air particulate matter (“light-absorbing yellow or brown carbon”):^[19] polycyclic aromatics and humic-like substances. Therefore, optically determined BC values must be considered as mass-equivalent values but not as absolute mass or concentration values. Moreover, most conventional optical methods such as aethalometry, integrating-sphere methods, and integrating-plate methods are based on the measurement of light extinction rather than absorption. As a consequence these methods require aerosol-composition-dependent calibrations or additional sample work-up processes to compensate for or minimize the influence of scattering aerosol components such as inorganic salts and acids on the measurement signal.^[67,69,70] Alternatively, photoacoustic spectroscopy allows direct measurements of light absorption by airborne aerosol particles, and during the past years several photoacoustic spectrometers have been developed and applied for the measurement of aerosol absorption coefficients and BC equivalent concentrations.^[71–73]

Among the few methods available for the characterization of the molecular and crystalline structures of BC and EC (graphite-like carbon proportion and degree of order) are high-resolution electron microscopy, X-ray diffraction, and Raman spectroscopy.^[59,74] These measurement techniques have revealed that the microstructure and spectroscopic properties of flame soot, diesel soot, and related carbonaceous materials depend on the processes and conditions of particle formation and aging. So far, however, these methods have been too labor-intensive for routine investigations of atmospheric aerosol samples, and their application in quantitative analyses remains to be proven.^[59] Nevertheless, recently developed measurement systems show promise for the quantification of graphite-like carbon and soot in aerosol filter samples by Raman spectroscopy.^[75,76]

2.2. Primary and Secondary Organic Aerosol Components

The total mass of organic air particulate matter (OPM), that is, the sum of organic aerosol (OA) components, is usually estimated by multiplication of OC with a factor of about 1.5–2, depending on the assumed average molecular composition and accounting for the contribution of elements other than carbon contained in organic substances (H, O, N, S, etc.).^[19,77] The only way, however, to determine the overall mass, molecular composition, physicochemical properties, and potential toxicity of OPM accurately is the identification and quantification of all relevant chemical components. Also trace substances can be hazardous to human health, and potential interferences of refractive and colored organic components in the determination of BC or EC can be assessed only to the extent to which the actual chemical composition of OPM is known.^[57,78]

Depending on their origin, OA components can be classified as primary or secondary. Primary organic aerosol (POA) components are directly emitted in the condensed phase (liquid or solid particles) or as semivolatile vapors, which are condensable under atmospheric conditions. The main sources of POA particles and components are natural and anthropogenic biomass burning (forest fires, slashing and burning, domestic heating), fossil-fuel combustion (domestic, industrial, traffic), and wind-driven or traffic-related suspension of soil and road dust, biological materials (plant and animal debris, microorganisms, pollen, spores, etc.), sea spray, and spray from other surface waters with dissolved organic compounds.

Secondary organic aerosol (SOA) components are formed by chemical reaction and gas-to-particle conversion of volatile organic compounds (VOCs) in the atmosphere, which may proceed through different pathways:

- a) new particle formation: formation of semivolatile organic compounds (SVOCs) by gas-phase reactions and participation of the SVOCs in the nucleation and growth of new aerosol particles;
- b) gas-particle partitioning: formation of SVOCs by gas-phase reactions and uptake (adsorption or absorption) by preexisting aerosol or cloud particles;

- c) heterogeneous or multiphase reactions: formation of low-volatility or nonvolatile organic compounds (LVOCs, NVOCs) by chemical reaction of VOCs or SVOCs at the surface or in the bulk of aerosol or cloud particles.

The formation of new aerosol particles from the gas phase generally proceeds through the nucleation of nanometer-sized molecular clusters and subsequent growth by condensation of condensable vapor molecules. Experimental evidence from field measurements and model simulations suggests that new particle formation in the atmosphere is most likely dominated by ternary nucleation of $\text{H}_2\text{SO}_4\text{--H}_2\text{O--NH}_3$ and subsequent condensation of SVOCs.^[79–81] Laboratory experiments and quantum chemical calculations indicate, however, that SVOCs might also play a role in the nucleation process ($\text{H}_2\text{SO}_4\text{--SVOC}$ complex formation).^[82] The actual importance of different mechanisms of particle nucleation and growth in the atmosphere has not yet been fully unraveled and quantified. In any case, the formation of new particles exhibits a strong and nonlinear dependence on atmospheric composition and meteorological conditions, may be influenced by ions and electric-charge effects, and competes with gas-particle partitioning and heterogeneous or multiphase reactions.^[83] Among the principal parameters governing secondary particle formation are temperature, relative humidity, and the concentrations of organic and inorganic nucleating and condensing vapors, which depend on atmospheric transport as well as local sources and sinks such as photochemistry and preexisting aerosol or cloud particles.^[54,56,79,80] The rate and equilibrium of SVOC uptake by aerosol particles depend on the SVOC-accommodation coefficients and on the particle surface area, bulk volume, and chemical composition (kinetics and thermodynamics of gas-particle partitioning).^[84]

Most earlier studies of SOA formation were focused on pathways a and b. Several recent studies indicate, however, that heterogeneous and multiphase reactions may also play an important role and contribute substantially to the overall atmospheric burden of OPM.^[19,85–88] The term “heterogeneous reaction” generally refers to reactions of gases at the particle surface, whereas the term “multiphase reaction” refers to reactions in the particle bulk involving species from the gas phase.

A variety of different reversible and irreversible mechanisms of acid-catalyzed condensation and radical-initiated oligo- or polymerization reactions involving organic and inorganic acids and photooxidants can lead to secondary formation of LVOCs and NVOCs of high molecular mass (SOA oligomers/polymers; Table 2). The actual atmospheric relevance and contributions of the different SOA formation pathways and involved chemical reaction mechanisms, however, still remain to be clarified.^[19,56]

Depending on local sources, meteorological conditions, and atmospheric transport and thus on location, season, and time of day, the composition of OPM can be dominated by POA or by SOA components. Recent studies indicate high abundance of POA in tropical air masses owing to intense biomass burning, whereas SOA from biogenic and anthropogenic emissions of precursor VOCs seems to dominate in

Table 2: Prominent organic aerosol components.

Substance Classes	Proportions ^[a]	Sources
aliphatic hydrocarbons	10 ⁻²	biomass, fossil-fuel combustion
aliphatic alcohols and carbonyls	10 ⁻²	biomass, SOA/aging
levoglucosan	10 ⁻¹	biomass burning
fatty acids and other alkanolic acids	10 ⁻¹	biomass, SOA/aging
aliphatic dicarboxylic acids	10 ⁻¹	SOA/aging
aromatic (poly-)carboxylic acids	10 ⁻¹	SOA/aging, soil/dust
multifunctional aliphatic and aromatic compounds (OH, CO, COOH)	10 ⁻¹	SOA/aging, soil/dust
polycyclic aromatic hydrocarbons (PAHs)	10 ⁻³	fossil-fuel combustion, biomass burning
nitro- and oxy-PAHs	10 ⁻³	fossil-fuel combustion, biomass burning, SOA/aging
proteins and other amino compounds	10 ⁻¹	biomass
cellulose and other carbohydrates	10 ⁻²	biomass
secondary organic oligomers/polymers and humic-like substances	10 ⁻¹	SOA/aging, soil/dust

[a] Characteristic magnitudes of the mass proportion in fine OPM.

mid-latitude air masses. On a global scale, the formation of SOA appears to be dominated by oxidation of biogenic VOCs (mostly by ozonolysis of terpenes)^[89] and to amount to at least 50% of POA emissions.^[56,90] In the atmosphere, POA and SOA components are mixed with each other, with BC/EC, and with inorganic aerosol components (externally and internally mixed aerosols).^[91] Moreover, both POA and SOA components can be efficiently transformed upon interaction with reactive trace gases and solar radiation (chemical aging, Section 3).

Hundreds of organic compounds have been detected in air particulate matter. Even in the most comprehensive investigations, however, only 10–40% of the OPM content estimated from OC measurements have been unambiguously identified on a molecular level. Prominent organic substance classes, characteristic magnitudes of their proportion in fine OPM (approximate upper limit of mass fraction), and their main sources are summarized in Table 2.^[1,4,19,29,56,92–96]

Several studies have shown that macromolecules such as cellulose and proteins (molecular mass ≥ 1 kDa) and other compounds with relatively high molecular mass (≥ 100 Da) such as humic-like substances (HULIS) account for large proportions of OPM and WSOC.^[19,62,97–101] Evidently, biopolymers and humic substances are emitted as POA components (soil and road dust, sea spray, biological particles), which may be modified by chemical aging and transformation in the atmosphere (e.g. formation of HULIS by oxidative degradation of biopolymers). On the other hand, organic compounds with high molecular mass can also originate from SOA formation by heterogeneous and multiphase reactions at the surface and in the bulk of atmospheric particles as outlined above (SOA oligomers/polymers).

For the identification and quantification of individual organic compounds, filter and impactor samples are usually extracted with appropriate solvents, and the extracts are analyzed by advanced instrumental or bioanalytical methods of separation and detection: gas and liquid chromatography; capillary electrophoresis; absorption and fluorescence spec-

troscopy; mass spectrometry; immunosorbent, enzyme, and dye assays; etc.^[29,57,62,92,95,102–105] Alternatively, deposited or suspended particles can be partially or fully vaporized by thermal or laser desorption and directly introduced into a gas chromatograph or spectrometer.^[1,20,25,26,32]

In recent studies nuclear magnetic resonance,^[16] Fourier-transform infrared spectroscopy,^[77] scanning transmission X-ray microscopy,^[106] and aerosol mass spectrometry^[107] were applied for efficient characterization and quantification of functional groups in OPM (alkyl, carbonyl, carboxyl, and hydroxy groups; C–C double bonds and aromatic rings). These methods give valuable insight into the overall

chemical composition, oxidation state, and reactivity of OPM, but they provide only limited information about the actual identity of the individual compounds, which are present in the complex mixture. The molecular mass and structure of organic compounds, however, are crucial parameters for their physicochemical and biological properties and thus for their climate and health effects (volatility, solubility, hygroscopicity, CCN and IN activity, bioavailability, toxicity, allergenicity; see Sections 3 and 4).

3. Chemical Reactivity and Water Interactions

Chemical reactions proceed at the surface and in the bulk of solid and liquid aerosol particles and can influence atmospheric gas-phase chemistry as well as the properties of atmospheric particles and their effects on climate and human health.^[1,4,84,108–116,117]

For example, aerosol chemistry leads to the formation of reactive halogen species, changes to reactive nitrogen compounds, and depletion of ozone—especially in the stratosphere, upper troposphere, and marine boundary layer.^[118–128] On the other hand, chemical aging of aerosol particles generally changes their composition, decreases their reactivity, increases their hygroscopicity and cloud condensation activity, and can change their optical properties.^[19,114,115,129–134]

Because of their high surface-to-volume ratio, fine aerosol particles can be very efficiently transformed upon interaction with solar radiation (photolysis) and reactive trace gases (oxidation, nitration, acid–base reactions, hydrolysis, condensation or radical-initiated oligomerization, etc.). For example, oxidation and nitration reactions lead to the formation or degradation of hazardous aerosol components,^[6,61,78,101] they cause artifacts upon collection and analysis of air particulate matter,^[1,19,30] and they play a major role in technical processes and devices for the control of combustion aerosol emissions.^[74,135–137] Moreover, the interaction with water can lead to structural rearrangements of solid aerosol particles, to the

formation of highly concentrated aqueous solution droplets (hygroscopic growth), and to the formation of cloud droplets and ice crystals (Section 3.2).

Atmospheric aerosol transformations and gas–particle interactions generally involve multiple physicochemical processes such as mass transport, phase transition, and chemical reactions at the interface or in the bulk of gas, liquid and solid phases, as illustrated in Figure 7. These multiphase processes are pivotal for the aerosol and cloud interactions and feedback loops outlined in Figures 1 and 3, and thus for the climate and health effects of atmospheric aerosols detailed below (Section 4).

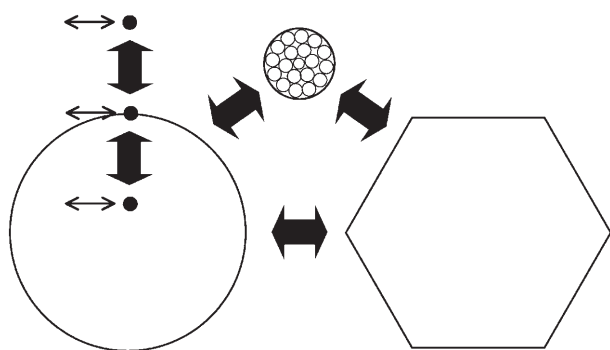


Figure 7. Schematic illustration of multiphase aerosol and cloud processes: mass transport and phase transitions of (semi-)volatile molecules between gas phase, aerosol particles, cloud droplets, and ice crystals (bold arrows); chemical reactions in the gas phase, at the particle surface, and in the particle bulk (thin arrows).

Efficient investigation, elucidation, and description of the interactions between multiple phases and chemical components of aerosols and clouds by laboratory experiments, field measurements, remote sensing, and model studies require consistent terminologies and universally applicable mathematical formalisms and physical parameters. However, the current understanding of the mechanisms and kinetics of mass transport, phase transitions, and chemical reactions in atmospheric aerosols and clouds is very limited. Besides a lack of experimental data, one of the limitations is that the formalisms applied in different studies have mostly been restricted to specific systems and boundary conditions: liquid water, ice, acid hydrates, soot, or mineral dust; fresh or aged surfaces; low or high reactant concentration levels, transient or (quasi-) steady-state conditions; limited selection of chemical species and reactions.^[84] The different and sometimes inconsistent rate equations, parameters, and terminologies make it hard to compare, extrapolate, and integrate the results of different studies over the wide range of reaction conditions relevant for the atmosphere, laboratory experiments, technical processes, and emission control.

A comprehensive kinetic model framework for aerosol and cloud surface chemistry and gas–particle interactions was recently proposed by Pöschl, Rudich, and Ammann (PRA).^[84] It allows the description of mass transport and chemical reactions at the gas–particle interface and the linking of surface processes with gas-phase and particle bulk processes

in aerosol and cloud systems with unlimited numbers of chemical components and physicochemical processes. The key elements and essential aspects of the PRA framework are:

- a simple and descriptive double-layer surface model (sorption layer and quasi-static layer);
- straightforward and additive flux-based mass balance and rate equations;
- clear separation of mass transport and chemical reactions;
- well-defined rate parameters (uptake and accommodation coefficients, reaction- and transport-rate coefficients);
- clear distinction between different elementary and multi-step transport processes (surface and bulk accommodation, etc.);
- clear distinction between different elementary and multi-step heterogeneous and multiphase reactions (Langmuir–Hinshelwood and Eley–Rideal mechanisms, etc.);
- mechanistic description of complex concentration and time dependence;
- flexible inclusion or omission of chemical species and physicochemical processes;
- flexible convolution or deconvolution of species and processes;
- full compatibility with traditional resistor model formulations.

Figure 8 illustrates the PRA model compartments and elementary processes at the gas–particle interface. The individual steps of mass transport are indicated by bold

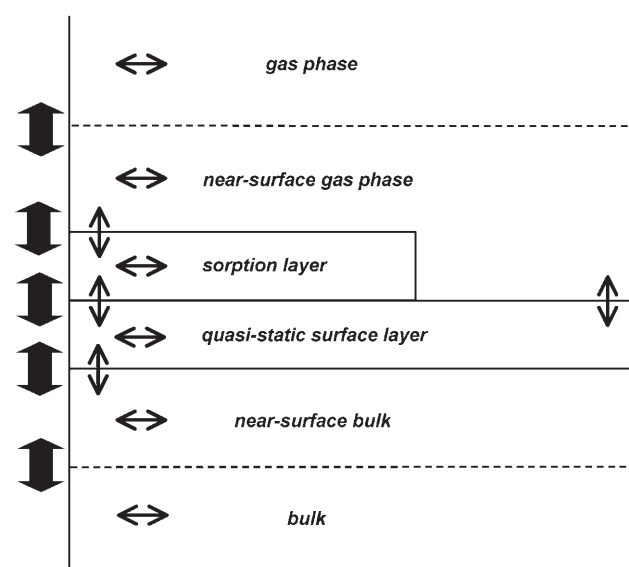


Figure 8. PRA framework model compartments, transport processes, and chemical reactions at the gas–particle interface (double-layer surface model): fluxes of diffusion in the gas phase and particle bulk, adsorption and desorption, transfer between sorption layer and quasi-static surface layer and between quasi-static surface layer and near-surface particle bulk indicated by vertical bold arrows on the left side; elementary chemical reactions between species in the same or in different model compartments indicated by horizontal and vertical thin arrows, respectively.^[84]

arrows beside the model compartments: gas-phase diffusion; reversible adsorption; mass transfer between sorption layer, quasi-static surface layer, and near-surface particle bulk; diffusion in the particle bulk. The thin arrows inside the model compartments represent different types of chemical reactions: gas-phase reactions; gas-surface reactions; surface-layer reactions; surface-bulk reactions; particle-bulk reactions.^[84] Exemplary practical applications and model calculations demonstrating the relevance of these aspects were presented in a companion paper.^[138]

The PRA framework is meant to serve as a common basis for experimental and theoretical studies to investigate and describe atmospheric-aerosol and cloud-surface chemistry and gas-particle interactions. In particular, it should support the following research activities: planning and design of laboratory experiments for the elucidation and determination of elementary processes and rate parameters; the establishment, evaluation, and quality assurance of comprehensive and self-consistent collections of kinetic parameters; and the development of detailed master mechanisms for process models and the derivation of simplified but yet realistic parameterizations for atmospheric and climate models in analogy to atmospheric gas-phase chemistry.^[89,139–143]

3.1. Chemical Transformation of Carbonaceous Aerosol Components

Organic aerosol components as well as the surface layers of BC or EC can react with atmospheric photooxidants (OH , O_3 , NO_3 , NO_2 , etc.), acids (HNO_3 , H_2SO_4 , etc.), water, and UV radiation. The chemical aging of OA components essentially follows the generic reaction pathways outlined in Figure 9 and tends to increase the oxidation state and water solubility of OC. In analogy to atmospheric gas-phase photochemistry of VOCs (methane, isoprene, terpenes, etc.),^[89,140,141] oxidation, nitration, hydrolysis, and photolysis transform hydrocarbons and derivatives with one or few functional groups into multifunctional hydrocarbon derivatives. The cleavage of organic molecules and release of SVOCs, VOCs, CO, or CO_2 can also lead to volatilization of OPM. On the other hand, oxidative modification and degradation of biopolymers may convert these into HULIS (analogous to the formation of humic substances in soil, surface water, and groundwater processes). Moreover, con-

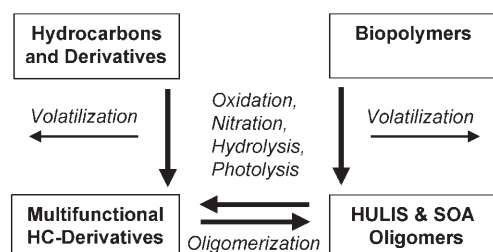


Figure 9. Generic reaction pathways for the atmospheric transformation (chemical aging) of organic aerosol components (left side: low molecular mass; right side: high molecular mass).

densation reactions and radical-initiated oligo- or polymerization can decrease the volatility of OA components and promote the formation of SOA particulate matter (SOA oligomers or HULIS; Table 2; Section 2.2).

The actual reaction mechanisms and kinetics, however, have been elucidated and fully characterized only for a small number of model reaction systems and components. So far, most progress has been made in the kinetic investigation and modeling of chemical reactions in cloud droplets.^[144,145] For the reasons outlined above, very few reliable and widely applicable kinetic parameters are available for organic reactions at the surface and in the bulk of liquid and solid aerosol particles.^[19,27,84,114,146,147]

Several studies have shown that surface reactions of organic molecules and black or elemental carbon with gaseous photooxidants such as ozone or nitrogen dioxide tend to exhibit nonlinear concentration dependence and competitive coadsorption of different gas-phase components, which can be described by Langmuir–Hinshelwood reaction mechanisms and rate equations.^[84,109,114,138,148]

An example of such reactions is the degradation of benzo[a]pyrene (BaP) on soot by ozone. BaP, a prominent air pollutant, is a polycyclic aromatic hydrocarbon (PAH) with the chemical formula $\text{C}_{20}\text{H}_{12}$ and consists of five six-membered aromatic rings. It is one of the most hazardous carcinogens and mutagens among the 16 priority PAH pollutants defined by the US Environmental Protection Agency (EPA). The main source of BaP in the atmosphere are combustion aerosols, and it resides to a large extent at the surface of soot particles.^[30,78,115]

Figure 10 shows pseudo-first-order rate coefficients for the degradation of BaP on soot by ozone at gas-phase mole fractions or volume mixing ratios (VMR) up to 1 ppm under dry conditions and in the presence of water vapor (relative humidity (RH) 25 %, 296 K, 1 atm). These and complementary results of aerosol flow tube experiments and model calculations indicate reversible and competitive adsorption of O_3 and H_2O , followed by a slower, rate-limiting surface reaction between adsorbed O_3 and BaP on the soot surface. The kinetic parameters determined from the displayed non-

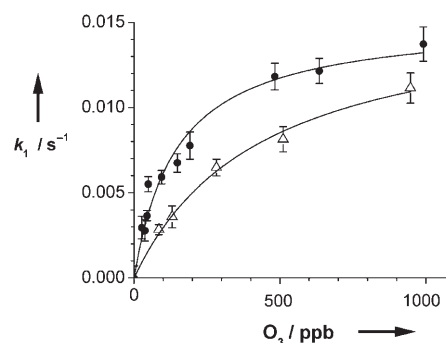


Figure 10. Pseudo-first-order rate coefficients (k_1) for the degradation of benzo[a]pyrene (BaP) on soot by ozone: measurement data from aerosol flow tube experiments under dry and humid conditions (symbols and error bars: arithmetic mean \pm standard deviation; full circles: RH < 1%; open triangles: RH \approx 25 %) and nonlinear least-squares-fit lines based on Langmuir–Hinshelwood rate equation.^[115]

linear least squares fits (maximum pseudo-first-order rate coefficients and effective Langmuir adsorption equilibrium constants) allow the prediction of the half-life (50 % decay time) of BaP on the surface of soot particles in the atmosphere. At typical ambient ozone VMR of about 30 ppb it would be only around 5 min under dry conditions and 15 min at 25 % RH.

Figure 11 illustrates the recovery ratio (RR) of BaP from fine air particulate matter (PM_{2.5}) collected with a regular

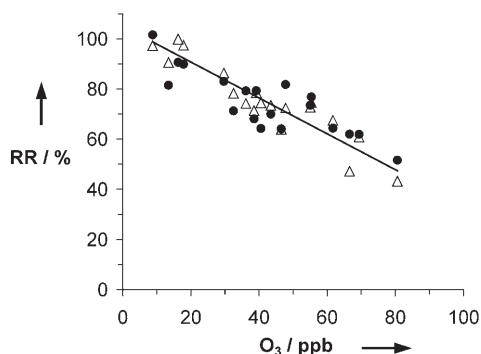


Figure 11. Recovery ratio for benzo[a]pyrene, BaP (full circles), and the sum of all particle-bound five- and six-ring US EPA priority PAH pollutants, PAH(5,6) (Δ), plotted against ambient ozone volume mixing ratio upon filter sampling of urban air particulate matter: measurement data points and linear least-squares fit.^[30]

filter sampling system from urban air at ambient ozone VMRs of up to 80 ppb (Munich, 2001/2002). The plotted recovery ratios refer to filter samples collected in parallel with a system that removes ozone and other photooxidants from the sample air flow by means of an activated carbon diffusion denuder.^[30] Thus deviations from unity represent the fraction of BaP degraded by reaction with ozone and other photooxidants from the sampled air during the sampling process, that is, the BaP loss by filter reaction sampling artifacts. The BaP recovery ratio is nearly identical to the recovery ratio of the sum of all particle-bound five- and six-ring US EPA priority PAH pollutants, PAH(5,6), and exhibits a negative linear correlation with ambient ozone. It decreases from 100 % at low ozone levels to 50 % at 80 ppb O₃, which is a characteristic concentration level for polluted urban air in summer. Similar correlations have been observed in experiments performed at different locations and with different filter sampling and denuder systems.^[30]

With regard to chemical kinetics, the linear correlation between PAH recovery ratio and O₃ VMR can be attributed to the near-linear dependence of the PAH degradation rate coefficient on O₃ at low VRMs (VMR \ll inverse of effective adsorption equilibrium constant; Figure 10).^[84,109,115,138] Moreover, it indicates efficient protection and shielding of the PAH on deposited particles from further decay by coverage with subsequently collected particulate matter (build-up of “filter cake”) on time scales similar to the half-life of PAH at the surface. Otherwise, the PAH recovery should be even lower

and the ozone concentration dependence should be less pronounced.

In any case, the sampling artifacts observed by Schauer et al. (2003) and illustrated in Figure 11 imply that the real concentrations of particle-bound PAH in urban air are up to 100 % higher than the measurement values obtained with simple filter-sampling systems (without activated carbon diffusion denuder or equivalent equipment) as applied for most atmospheric research and air-pollution-monitoring purposes.^[30,78,115] Clearly also other OA components with similar or higher reactivity towards atmospheric oxidants (e.g. alkenes) are prone to similar or even stronger sampling artifacts, which have to be avoided or at least minimized and quantified for accurate and reliable determination of atmospheric aerosol composition and properties. These and other potential sampling and analytical artifacts caused by reactive transformation of fine air particulate matter have to be taken into account not only in atmospheric and climate research activities, but also in air-pollution control. In particular, the control and enforcement of emission limits and ambient threshold level values for OA components which pose a threat to human health (Section 4.2) require the development, careful characterization and validation, and correct application of robust analytical techniques and procedures.^[78]

As far as atmospheric aerosol cycling and feedback loops are concerned (Figures 1 and 3), chemical aging and oxidative degradation of organic compounds present on the surface and in the bulk generally makes aerosol particles more hydrophilic or hygroscopic and enhances their ability to act as CCN. Besides their contribution to the water-soluble fraction of particulate matter, partially oxidized organics can act as surfactants and influence the hygroscopic growth, CCN, and IN activation of aerosol particles (Section 3.2).

The chemical reactivity of carbonaceous aerosol components also plays an important role in technical applications for the control of combustion aerosol emissions. For example, the lowering of emission limits for soot and related diesel exhaust particulate matter (DPM) necessitates the development and implementation of efficient exhaust-treatment technologies such as diesel particulate filters or particle traps with open deposition structures. These systems generally require regeneration by oxidation and gasification of the soot deposits in the filter or catalyst structures. Usually the regeneration is based on discontinuous oxidation by O₂ at high temperatures (> 500 °C) or continuous oxidation by NO₂ at moderate exhaust temperatures (200–500 °C).^[74,135–137,149] Efficient optimization of the design and operating conditions of such exhaust-treatment systems requires comprehensive kinetic characterization and mechanistic understanding of the chemical reactions and transport processes involved. Recent investigations have shown that the oxidation and gasification of diesel soot by NO₂ at elevated concentrations and temperatures (up to 800 ppm NO₂ and 500 °C) follow a similar Langmuir–Hinshelwood reaction mechanism as the oxidation of BaP on soot by O₃ at ambient concentrations and temperature (up to 1 ppm O₃ and 30 °C).^[115,148,149]

3.2. Restructuring, Phase Transitions, Hygroscopic Growth, and CCN/IN Activation of Aerosol Particles upon Interaction with Water Vapor

When water vapor molecules interact with aerosol particles, they can be adsorbed to the surface of the particles or absorbed into the bulk of the particles. For particles consisting of water-soluble material, the uptake of water vapor can lead to aqueous solution droplet formation and a substantial increase in the particle diameter (hygroscopic growth) even at low relative humidities ($RH < 100\%$; atmospheric gas phase water partial pressure $<$ equilibrium vapor pressure of pure liquid water).^[8]

At water vapor supersaturation ($RH > 100\%$) aerosol particles can act as nuclei for the formation of liquid cloud droplets (cloud condensation nuclei, CCN). For the formation of water droplets from a homogenous gas phase devoid of aerosol particles supersaturations of up to several hundred percent would be required (thermodynamic barrier for the homogenous nucleation of a new phase). In the atmosphere, however, water vapor supersaturations with respect to liquid water generally remain below 10% and mostly even below 1%, because aerosol particles induce heterogeneous nucleation, condensation, and cloud formation. At low temperatures or high altitudes clouds consist of mixtures of liquid water droplets and ice crystals, or entirely of ice crystals. The formation of ice crystals is also induced by preexisting aerosol particles, so-called ice nuclei (IN), as detailed below. Ice nucleation in clouds usually requires temperatures well below 0°C, which can lead to high water vapor supersaturations with respect to ice.^[8,150–155]

The minimum supersaturation at which aerosol particles can be effectively activated as CCN or IN, respectively, is called critical supersaturation. It is determined by the physical structure and chemical composition of the particles and generally decreases with increasing particle size. For insoluble CCN the critical supersaturation depends on the wettability of the surface (contact angle of liquid water), and for partially or fully soluble CCN it depends on the mass fraction, hygroscopicity, and surfactant activity of the water-soluble particulate matter.^[8,53,55,156,157]

The nucleation of ice crystals on atmospheric aerosol particles can proceed through different pathways or modes. In the deposition mode, water vapor is adsorbed and immediately converted into ice on the surface of the IN (deposition or sorption nuclei). In the condensation freezing mode the aerosol particles act first as CCN and induce the formation of supercooled aqueous droplets, which freeze later on (condensation freezing nuclei). In the immersion mode the IN are incorporated into preexisting aqueous droplets and induce ice formation upon cooling (immersion nuclei). In the contact mode, freezing of a supercooled droplet is initiated upon contact with the surface of the IN (contact nuclei). Obviously, the IN activity of aerosol particles depends primarily on their surface composition and structure, but condensation and immersion freezing can also be governed by water-soluble bulk material.^[8,154,158–164]

Most water-soluble aerosol components are hygroscopic and absorb water to form aqueous solutions at $RH < 100\%$.

The phase transition of dry particle material into a saturated aqueous solution is called deliquescence and occurs when a substance-specific RH threshold value (deliquescence relative humidity, DRH) is exceeded. The reverse transition and its RH threshold value are called efflorescence and efflorescence relative humidity (ERH), respectively. The hygroscopic growth and CCN activation of aqueous solution droplets can be described by the so-called Köhler theory, which combines Raoult's law or alternative formulations for the activity of water in aqueous solutions and the Kelvin equation for the dependence of vapor pressure on the curvature and surface tension of a liquid droplet.^[8,24,53,55,156,165–169]

Figure 12a shows a typical example of the hygroscopic growth of water-soluble inorganic salts contained in air particulate matter: the hygroscopic growth curve (humidogram) of pure NaCl aerosol particles with dry particle diameters of 100 nm measured in a hygroscopicity tandem differential mobility analyzer (H-TDMA) experiment at relative humidities of up to 95%. Upon hydration (increase of RH) the crystalline NaCl particles undergo a deliquescence transition at $DRH \approx 75\%$. The water uptake and dependence of the aqueous solution droplet diameter on RH agree very well with Köhler theory calculations, which are based on a semiempirical ion interaction parameterization of water activity and account for the effects of particle-shape transformation (cubic crystals and spherical droplets, mobility and mass equivalent diameters).^[24] The hysteresis branch measured upon dehydration (decrease of RH) is due to the existence of solution droplets in a metastable state of NaCl supersaturation ($ERH < RH < DRH$). The efflorescence transition, that is, the formation of salt crystals and evaporation of the liquid water, occurs at $ERH \approx 40\%$.

Figure 12b displays the hygroscopic growth curve of aerosol particles composed of pure bovine serum albumin (BSA) as a model for globular proteins and similar organic macromolecules. The hygroscopic growth is much less pronounced than for inorganic salts but still significant, with deliquescence and efflorescence transitions at $DRH \approx ERH \approx 40\%$ (conversion of dry protein particles into saturated aqueous solution or gel-like droplets, v.v.) and no significant deviations between hydration and dehydration (no hysteresis effect). The dependence of the deliquesced particle diameter on RH is in good agreement with Köhler theory calculations based on a simple osmotic pressure parameterization of water activity, which has been derived under the assumption that the dissolved protein macromolecules behave like inert solid spheres.^[24]

Figure 12c shows the hygroscopic growth curve of internally mixed NaCl–BSA particles (mass ratio 1:1) with dry particle diameters of approximately 100 nm. The mixed aerosol particles have been generated in full analogy to the pure NaCl and pure BSA particles (nebulization of an aqueous solution). Upon hydration, however, the particles exhibit a significant decrease of the measured (mobility equivalent) diameter as the relative humidity approaches the deliquescence threshold ($DRH \approx 75\%$). The observed minimum diameter is about 10% smaller than the initial diameter, indicating high initial porosity of the particles (envelope void

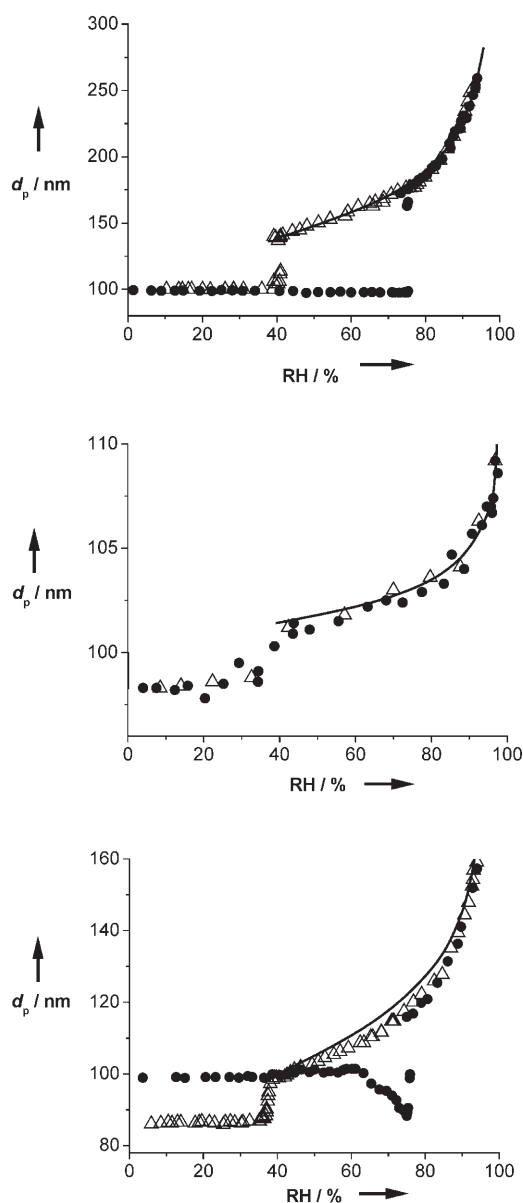


Figure 12. Hygroscopic growth curves for a) pure NaCl salt particles, b) pure BSA protein particles, and c) internally mixed BSA–NaCl protein–salt particles: data points measured upon hydration (●) and dehydration (△) in H-TDMA aerosol experiments; solid lines represent Köhler theory calculations based on NaCl ion interaction and BSA osmotic pressure parameterizations for water activity.^[24]

fraction $\approx 30\%$) and strong restructuring upon humidification. Upon dehydration the efflorescence threshold is lower than for pure NaCl (ERH $\approx 37\%$ vs. 40%), indicating that the protein macromolecules inhibit the formation of salt crystals and enhance the stability of supersaturated salt solution droplets. The particle diameters observed after efflorescence essentially equal the minimum diameter observed prior to deliquescence. The hygroscopic growth of the deliquesced particles (aqueous solution droplets) is in fair agreement with Köhler theory calculations based on the observed minimum diameter rather than the initial diameter and on the assumption of simple solute additivity (linear combination

of NaCl ion interaction and BSA osmotic pressure parameterizations of water activity).^[24] These and complementary measurement and modeling results can be explained by the formation of porous agglomerates due to ion–protein interactions and electric charge effects on the one hand, and by compaction of the agglomerate structure due to capillary condensation and surface tension effects on the other.

Depending on their origin and conditioning, aerosol particles containing inorganic salts and organic (macro-) molecules can have complex and highly porous microstructures, which are influenced by electric charge effects and interactions with water vapor. Proteins and other surfactants tend to be enriched at the particle surface and form an envelope that can inhibit the access of water vapor to the particle core and lead to kinetic limitations of hygroscopic growth, phase transitions, and CCN and IN activation. Formation and effects of organic surfactant films on sea salt particles have recently been discussed by O'Dowd et al.^[170] These and other effects of (nonlinear) interactions between organic and inorganic aerosol components have to be elucidated further and considered for consistent analysis of measurement data from laboratory experiments and field measurements and for reliable modeling of atmospheric aerosol processes (Figures 1 and 3).

Structural rearrangements, hygroscopic growth, phase transitions, and CCN and IN activation of aerosol particles interacting with water vapor are not only important for the formation and properties of clouds and precipitation (number density and size of cloud droplets and ice particles; temporal and spatial distribution and intensity of precipitation). They influence also the chemical reactivity and aging of atmospheric particles (accessibility of particle components to reactive trace gases and radiation), their optical properties (absorption and scattering cross-sections), and their health effects upon inhalation into the human respiratory tract (deposition efficiency and bioavailability). Therefore, the water interactions of particles with complex chemical composition are widely and intensely studied in current aerosol, atmospheric, and climate research. So far, however, their mechanistic and quantitative understanding is still rather limited, especially with regard to carbonaceous components.^[3,8,19,55,56,154,169,171–176]

4. Climate and Health Effects

Anthropogenic emissions are major sources of atmospheric aerosols. In particular, the emissions of particles and precursor gases from biomass burning and fossil-fuel combustion have massively increased since preindustrial times and account for a major fraction of fine air particulate matter in polluted urban environments as well as in the global atmosphere (carbonaceous components, sulfates, etc.).^[1,2,4,9,177–183] Numerous studies have shown that both natural and anthropogenic aerosols have a strong impact on climate and human health. Due to the limited knowledge of aerosol sources, composition, properties, and processes outlined above, however, the actual effects of aerosols on climate and health are still far from being fully understood and

quantified. Some of the most important aspects and recent developments will be addressed in the following sections.

4.1. Direct and Indirect Aerosol Effects on Climate

Aerosol effects on climate are generally classified as direct or indirect with respect to radiative forcing of the climate system. Radiative forcings are changes in the energy fluxes of solar radiation (maximum intensity in the spectral range of visible light) and terrestrial radiation (maximum intensity in the infrared spectral range) in the atmosphere, induced by anthropogenic or natural changes in atmospheric composition, Earth surface properties, or solar activity. Negative forcings such as the scattering and reflection of solar radiation by aerosols and clouds tend to cool the Earth's surface, whereas positive forcings such as the absorption of terrestrial radiation by greenhouse gases and clouds tend to warm it (greenhouse effect).^[2] Figure 13 illustrates the

and terrestrial radiation, clouds and precipitation, general circulation and hydrological cycle, and with natural and anthropogenic aerosol and trace gas sources on global and regional scales. On microscopic and molecular scales, each of the interactions outlined in Figure 13 comprises a multitude of physicochemical processes that depend on atmospheric composition and meteorological conditions and are largely not quantitatively characterized. Thus the actual climate system responses and feedback to natural or anthropogenic perturbations such as industrial and traffic-related greenhouse gas and aerosol emissions, volcanic eruptions, etc. are highly uncertain. In many cases, even the sign or direction of the feedback effect is unknown, that is, it is not clear whether a perturbation will be reinforced (positive feedback) or dampened (negative feedback).

For example, enhanced deposition and uptake of aerosol particles and trace gases on vegetation, soil, or surface water can lead to an increase or decrease in biogenic POA and SOA precursor emissions, depending on the fertilizing, toxic, or

reproductive biological activity of the aerosol and trace gas components. The increase in atmospheric CO₂ and global warming is expected to enhance photosynthesis, biogenic emissions of VOC, and the formation of SOA particles, which may act as CCN, increase cloudiness, and lead to a cooling effect (negative feedback).^[54] On the other hand, the negative feedback mechanism could be counteracted by temperature-related biological stress and eutrophication effects which may lead to a decrease in photosynthesis, biomass production, VOC emissions, SOA formation, and cloudiness, and further enhance global warming (positive feedback). In any case, feedback effects of this kind and the influence of SOA formation on CCN and IN concentration are determined not only by VOC emissions but also by the photochemical transformation of VOCs into SVOCs and LVOCs/

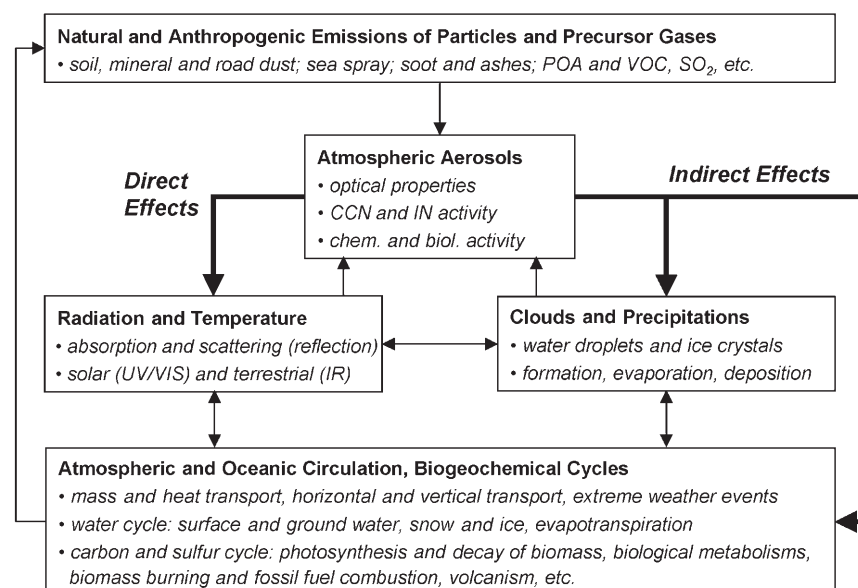


Figure 13. Direct and indirect aerosol effects and major feedback loops in the climate system.

distinction between direct and indirect aerosol effects and some major feedback loops in the climate system. Direct effects result from the scattering and absorption of radiation by aerosol particles, whereas indirect effects result from their CCN and IN activity (influence on clouds and precipitation), or from their chemical and biological activity (influence on aerosol and trace gas emissions and transformation).

The optical properties relevant for the direct effects (scattering and absorption coefficient or extinction cross-section and single scattering albedo, etc.) as well as the CCN, IN, chemical and biological activities relevant for indirect effects are determined by aerosol particle size, structure, and chemical composition. Thus they are strongly influenced by the atmospheric processes outlined above (coagulation, chemical transformation, water interactions).

The climate feedback loops illustrated in Figure 13 involve the interaction of atmospheric aerosols with solar

NVOCs, respectively, and their contribution to the growth of preexisting particles or to the formation of new particles. As outlined above, these processes strongly depend on atmospheric composition and meteorological conditions.

An increase in atmospheric CCN and IN concentrations in the atmosphere can have different effects on the formation and properties of liquid water, ice, and mixed-phase clouds and precipitation. Among them are the so-called cloud albedo or Twomey effect (more-numerous and smaller cloud particles reflect more solar radiation), cloud lifetime effect (smaller cloud particles decrease the precipitation efficiency), thermodynamic effect (smaller cloud droplets delay the onset of freezing), and glaciation effect (more IN increase the precipitation efficiency). These and related effects of aerosol, cloud, precipitation, and radiation interactions influence the regional and global radiative energy balance and hydrological cycle as well as the temperature, dynamics, and general

circulation of the atmosphere and oceans.^[2,184–187] Moreover, they can promote extreme weather events (intense rain, hail, and thunderstorms).^[188] A recent review article by Lohmann and Feichter (2005)^[3] provides an overview of indirect aerosol effects, their estimated magnitude, and climatic implications.

Overall, the current aerosol radiative forcing relative to that in preindustrial times is estimated to be around -1 to -2 W m^{-2} , as opposed to a greenhouse gas forcing of about $+2.4 \text{ W m}^{-2}$.^[2,3,187] Owing to the limited understanding of the underlying physicochemical processes, however, it is still unclear if clouds provide a positive or negative feedback to an increase in atmospheric carbon dioxide and other greenhouse gases. The uncertainties of aerosol, cloud, and precipitation interactions and feedback effects are among the main reasons for the high uncertainty of climate sensitivities and for the projected global mean surface temperature increase over the next century ($1\text{--}6^\circ\text{C}$ or more).^[2,3,56]

4.2. Aerosol Health Effects and Air Quality

Numerous epidemiological studies show that fine air particulate matter and traffic-related air pollution are correlated with severe health effects, including enhanced mortality, cardiovascular, respiratory, and allergic diseases.^[5,189–192] Moreover, toxicological investigations in vivo and in vitro have demonstrated substantial pulmonary toxicity of model and real environmental aerosol particles, but the biochemical mechanisms and molecular processes that cause the toxicological effects such as oxidative stress and inflammatory response have not yet been resolved. Among the parameters and components potentially relevant for aerosol health effects are the specific surface, transition metals, and organic compounds.^[5,193–195] Some of the possible mechanisms by which air particulate matter and other pollutants may affect human health are summarized in Table 3.

Table 3: Possible mechanisms by which aerosol particles and other air pollutants may cause adverse health effects.^[5]

pulmonary inflammation induced by PM or O ₃
free radical and oxidative stress generated by transition metals or organic compounds (e.g. PAHs)
covalent modification of key intracellular proteins (e.g. enzymes)
inflammation and innate immune effects induced by biological compounds such as endotoxins and glucans
stimulation of nociceptor and autonomic nervous system activity regulating heart-rate variability and airway reactivity
adjuvant effects in the immune system (e.g. DPM and transition metals enhancing responses to common environmental allergens)
procoagulant activity by ultrafine particle accessing the systemic circulation
suppression of normal defense mechanisms (e.g. suppression of alveolar macrophage functions)

Ultrafine particles ($d_p < 100 \text{ nm}$) are suspected to be particularly hazardous to human health, because they are sufficiently small to penetrate the membranes of the respiratory tract and enter the blood circulation or be transported along olfactory nerves into the brain.^[196–198] Neither for ultrafine nor for larger aerosol particles, however, it is clear which physical and chemical properties actually determine their adverse health effects (particle size, structure, number, mass concentration, solubility, chemical composition, and individual components, etc.).

Particularly little is known about the relations between allergic diseases and air quality. Nevertheless, traffic-related air pollution with high concentration levels of fine air particulate matter, nitrogen oxides, and ozone is one of the prime suspects besides non-natural nutrition and excessive hygiene practices, which may be responsible for the strong increase of allergies in industrialized countries over the past decades.^[5,199–201] The most prominent group of airborne allergens are protein molecules, which account for up to 5 % of urban air particulate matter. They are not only contained in coarse biological particles such as pollen grains (diameter $> 10 \mu\text{m}$) but also in the fine fraction of air particulate matter, which can be explained by fine fragments of pollen, microorganisms, or plant debris and by mixing of proteins dissolved in rain water with fine soil and road dust particles.^[98,101,202]

A molecular rationale for the promotion of allergies by traffic-related air pollution has been proposed by Franze et al. (2003; 2005),^[101,102] who found that proteins including birch pollen allergen Bet v1 are efficiently nitrated by polluted urban air. The nitration reaction converts the natural aromatic amino acid tyrosine into nitrotyrosine and proceeds particularly fast at elevated concentrations of NO₂ and O₃ (so-called photo-smog or summer smog conditions), most likely involving nitrate radicals (NO₃) as reactive intermediates. From biomedical and immunological research it is known that protein nitration occurs upon inflammation of biological tissue, where it may serve to mark foreign proteins and guide the immune system. Moreover, conjugates of proteins and peptides with nitroaromatic compounds were found to evade immune tolerance and boost immune responses, and post-translational modifications generally appear to enhance the allergenicity of proteins.^[101] Thus the inhalation of aerosols containing nitrated proteins or nitrating reagents is likely to trigger immune reactions, promote the genesis of allergies, and enhance the intensity of allergic diseases and airway inflammations. This hypothesis is supported by first results of ongoing biochemical experiments with nitrated proteins.^[203]

By means of newly developed enzyme immunoassays, nitrated proteins have been detected in urban road and window dust as well as in fine air particulate matter, exhibiting degrees of nitration of up to 0.1 %. Upon exposure of birch pollen extract to heavily polluted air at a major urban traffic junction and to synthetic gas mixtures containing NO₂ and O₃ at concentration levels characteristic for intense summer smog, the degrees of nitration increased up to 20 %. The experimental results indicate that Bet v1 is more easily nitrated than other proteins, which might be an explanation why it is a particularly strong allergen.^[101] If the ongoing

biochemical experiments and further studies confirm that protein nitration by nitrogen oxides and ozone is indeed an important link between air pollution, airway inflammations, and allergies, the spread and enhancement of these diseases could be counteracted by an improvement in the air quality and a decrease in emission limits for nitrogen oxides and other traffic-related air pollutants. Moreover, it might be possible to develop pharmaceuticals against the adverse health effects of nitrated proteins.

Efficient control of air quality and related health effects requires a comprehensive understanding of the identity, sources, atmospheric interactions, and sinks of hazardous pollutants. Without this understanding, the introduction of new laws, regulations, and technical devices for environmental protection runs the risk of being ineffective or even of causing more harm than good through unwanted side effects.

For example, epidemiological evidence for adverse health effects of fine and ultrafine particles has led to a lowering of present and future emission limits for soot and related DPM.^[137, 198, 204–206] For compliance with these emission limits, different particle filter or trapping and exhaust-treatment technologies have been developed and are currently being introduced into diesel vehicles. Depending on the design of the particle filter or trap and catalytic converter systems, their operation can lead to substantial excess NO₂ emissions.^[148] If, however, elevated NO₂ concentrations and the nitration of proteins indeed promote allergies, such systems could reduce respiratory and cardiovascular diseases related to soot particles but at the same time enhance allergic diseases. Moreover, elevated NO₂ concentrations and incomplete oxidation of soot in exhaust filter systems could also increase the emissions of volatile or semivolatile hazardous aerosol components such as nitrated PAH derivatives.^[61, 78] Thus an effective mitigation of the adverse health effects of diesel engine exhaust may require the introduction of advanced catalytic converter systems that minimize the emissions of both particulate and gaseous pollutants (soot, PAH and PAH derivatives, nitrogen oxides, etc.) rather than simple particle filters.

In any case, comprehensive investigations, understanding, and control of aerosol health effects need to consider both the particulate and gaseous components of aerosols as well as their chemical reactivity and aging.^[78]

5. Summary and Outlook

Scientific investigations and reports of atmospheric aerosols date back as far as the 18th century, and since then it has become increasingly clear that aerosol particles are of major importance for atmospheric chemistry and physics, the hydrological cycle, climate, and human health.^[207] Motivated by global change and adverse health effects of traffic-related air pollution, aerosol research has been intensified increasingly over the past couple of decades.

These activities have led to a fairly comprehensive conceptual understanding of atmospheric aerosol sources, composition, properties, interactions, and effects on climate. The parameters required for a quantitative description of the

underlying physicochemical processes, however, are generally still uncertain by factors of two or more, which implies uncertainties of an order of magnitude for most effects involving multiple competitive or sequential processes.

In some cases (e.g. particle nucleation and reactive gas uptake), even the basic parameters are uncertain by orders of magnitude. Consequently, model calculations of atmospheric aerosol effects on future climate have to be regarded as sensitivity studies with more or less reliable qualitative and semiquantitative results and implications, rather than reliable quantitative predictions. In particular, interactions and feedback responses between aerosols and clouds, the hydrological cycle, and the biosphere are difficult to quantify with the currently available information. Regardless of the rapid increase in numerical simulation capacities, this situation can hardly change before the basic physicochemical processes and properties of atmospheric aerosol particles have been elucidated to an extent comparable to the present state of knowledge of atmospheric gas-phase chemistry (universally applicable and validated master mechanisms, rate coefficients, structure–reactivity relationships, etc.).

Outstanding open questions and research aims for the elucidation of aerosol effects relevant to the science and policy of global change have been outlined in several recent monographs, reviews, and research articles.^[2, 3, 54, 79, 80, 84] Among these are the quantification, mechanistic elucidation, and kinetic characterization of the following processes: formation of new particles and secondary organic aerosols; emission of primary organic aerosol components and black or elemental carbon; aging and deposition of aerosol particles; activation of cloud condensation and ice nuclei. As far as chemical transformations, heterogeneous and multiphase reactions, and gas–particle interactions of aerosols and clouds are concerned, one of the most important prerequisites for efficient further investigation and scientific progress is the establishment of a common basis of consistent, unambiguous, and universally applicable terminologies, model formalisms, and kinetic and thermodynamic parameters.

With regard to atmospheric aerosol effects on human health not only the quantitative but also the qualitative and conceptual understanding is very limited. Epidemiological and toxicological studies indicate strong adverse health effects of fine and ultrafine aerosol particles as well as gaseous air pollutants, but the causative relations and mechanisms are hardly known.^[5, 192] Their elucidation, however, is required for the development of efficient strategies for air-quality control and medical treatment of related diseases that will enable the minimization of adverse aerosol health effects at minimum social and economic costs.

Particularly little is known about the relationship between allergic diseases and air pollution and the interactions between natural aeroallergens and traffic-related pollutants. Several studies have shown synergistic and adjuvant effects of diesel particulate matter, O₃, NO₂, and allergenic pollen proteins, but the specific chemical reactions and molecular processes responsible for these effects have not yet been clearly identified. Recent investigations indicate that the nitration of allergenic proteins by polluted air may play an important role. Nitrated proteins are known to stimulate

immune responses, and they could promote the genesis of allergies, enhance allergic reactions, and influence inflammatory processes, which is confirmed by the results of ongoing biochemical investigations.^[101,203]

For efficient elucidation and abatement of adverse aerosol health effects, the knowledge of atmospheric and biomedical aerosol research should be integrated to formulate plausible hypotheses that specify potentially hazardous chemical substances and reactions on a molecular level. These hypotheses have to be tested in appropriate biochemical and medical studies to identify the most relevant species and mechanisms of interaction and to establish the corresponding dose-response relationships. Ultimately, the identification and characterization of hazardous aerosol components and their sources and sinks (emission, transformation, deposition) should allow the optimization of air-pollution control and medical treatment of aerosol effects on human health.

6. Appendix

List of Abbreviations, Acronyms, and Symbols

BaP	benzo[a]pyrene
BC	black carbon
BSA	bovine serum albumin
CCN	cloud condensation nucleus
CE	capillary electrophoresis
CI	chemical ionization
d_p	particle diameter
$dN/d(\log d_p)$	particle number size distribution function
DMA	differential mobility analyzer
DPM	diesel exhaust particulate matter
DRH	deliquescence relative humidity
EC	elemental carbon
EI	electron impact ionization
ELPI	electrical low-pressure impactor
EPA	Environmental Protection Agency
ERH	efflorescence relative humidity
ESI	electrospray ionization
HC	hydrocarbon
H-TDMA	hygroscopicity tandem differential mobility analyzer
HULIS	humic-like substances
IC	ion chromatography
IN	ice nucleus
k_1	(pseudo-)first-order rate coefficient
LDI	laser desorption ionization
LVOC	low-volatility organic compound
MWSOC	macromolecular water-soluble organic carbon
NVOC	nonvolatile organic compound
OA	organic aerosol
OC	organic carbon
OPM	organic particulate matter
PAH	polycyclic aromatic hydrocarbon
PAH(5,6)	polycyclic aromatic hydrocarbons consisting of five or six aromatic rings
PM	particulate matter

PM2.5 (1 or 10)	particulate matter of particles with aerodynamic diameters $\leq 2.5 \mu\text{m}$ (1 or 10 μm)
POA	primary organic aerosol
PRA	Pöschl, Rudich, Ammann (2005)
QCM	quartz crystal microbalance
RH	relative humidity
RR	recovery ratio
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SIMS	secondary ion mass spectrometry
SMPS	scanning mobility particle sizer
SOA	secondary organic aerosol
SPE	solid-phase extraction
SVOC	semivolatile organic compound
TC	total carbon
TEM	transmission electron microscopy
TEOM	tapered element oscillating microbalance
VMR	volume mixing ratio
VOC	volatile organic compound
WSOC	water-soluble organic carbon

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