



Carbonaceous Aerosol Components: Properties, Interactions, Climate and Health Effects

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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. Moreover, airborne particles play an important role for the spread of biological organisms, reproductive materials, and pathogens (pollen, bacteria, spores, viruses, etc.), and they can cause or enhance respiratory, cardiovascular, infectious, and allergic diseases. The primary parameters which determine these effects are particle size, structure, and composition. The concentration and size distribution of aerosol particles in the troposphere, however, are temporally and spatially highly variable, and the knowledge of their physicochemical properties and transformation is very limited.

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

and suitability of BC, EC, and OC data for the determination of mass balances and physicochemical properties of air particulate matter (“How black is black carbon?”). Besides different types of graphite-like materials there are at least two classes of organics which can contribute to the absorption of visible light by air particulate matter: polycyclic aromatics and humic-like substances. Hundreds of organic compounds have been determined, but only 10-40 % of the total organic particulate matter (OPM) in air have been identified at a molecular level.

Moreover, most organics interact with atmospheric photooxidants and water, but the mechanisms and kinetic parameters of mass transport and chemical reactions are hardly known. For example, oxidation and nitration reactions lead to the formation or degradation of hazardous aerosol components, they cause artifacts upon collection and analysis of air particulate matter, and they play a major role in technical processes and devices for the control of combustion aerosol emissions. 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. Atmospheric aerosol transformations and gas-particle interactions generally involve multiple physicochemical processes like mass transport, phase transition, and chemical reaction at the interface or in the bulk of gas, liquid and solid phases. Besides a lack of experimental data, one of the limitations of our current understanding of aerosol chemistry 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. 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.

Motivated by global change and adverse health effects of traffic-related air pollution, aerosol research has been increasingly intensified over the past couple of decades. This has 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 order of magnitude uncertainties for most effects involving multiple competitive or sequential processes. In some cases like 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 stud-

ies with more or less reliable qualitative and semi-quantitative 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 of 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 mechanisms, rate coefficients, and structure-reactivity relationships, etc.).

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 ultra-fine aerosol particles as well as gaseous air pollutants, but the causative relations and mechanisms are hardly known. Particularly little is known about the relations 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 unambiguously 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. In any case, substantial progress in the identification and characterization of hazardous aerosol components and their sources, sinks, and dose-response relationships will be required for the development of efficient strategies of air quality control.

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