Chapter 1

Editors' Perspective on Multiphase Chemistry in the Atmosphere

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The chapter outlines authors' view on the importance of multiphase chemistry in the atmosphere. The chapter starts with a short description of the development of atmospheric chemistry from gas-phase spectroscopy and kinetics into a highly interdisciplinary research on complex multiphase processes. Despite the impressive progress over the years in our understanding of multiphase processes, the air pollution and climate problems are far from being solved. Further research on multiphase chemical reactions and the interactions across phases is needed in order to understand the properties and effects of complex mixtures of trace gases and particles that surround us.

Some of us can still remember the days when science was broken up into traditional areas, with well-defined boundaries between physics, chemistry, biology, medicine, etc. As scientific progress has been made, and more challenging problems have been recognized and investigated, researchers have shifted into areas that creatively combine multiple traditional fields. In atmospheric chemistry, the transition to a multidisciplinary research approach naturally happened decades ago. The early atmospheric chemistry research focused on understanding problems that are relatively simple by today's standards, for example, studying photochemistry and kinetics of small gas-phase molecules such as aldehydes and ketones (*1*). As our understanding of atmospheric chemistry grew, more challenging problems involving chemistry occurring on surfaces and in condensed-phases had to be attacked. The current research frontier in atmospheric chemistry involves understanding the behavior of molecules that exist and react in different phases. The term "multiphase chemistry" was coined by atmospheric scientists to denote "chemical reactions, transport processes, and transformations between gaseous, liquid, and solid matter" (*2*). The inherent complexity of multiphase processes has motivated the development of novel platforms for laboratory and field measurements, as well as advanced modeling approaches.

The chemistry of the atmosphere is driven by trace chemical species that can be found in the gas phase, solid and liquid particles, cloud and fog droplets, and also on environmental surfaces that are in direct contact with the atmosphere. Chemical species that appear in the atmosphere as a result of human activities, and have adverse effects on the human health and ecosystems, are classified as air pollutants. Air pollution has been a problem in cities for hundreds of years, and it has become an acute problem with rapid industrialization and growth of megacities (*3*). One of the most famous air pollution episodes is the Great Smog of London in 1952, which was a result of smoke and a stagnant air mass over the city, resulting in thousands of deaths over several days (*4*). The presence of air pollutants in the atmosphere affects not only humans but also the entire biosphere. In fact, the research into the hazardous chemical compounds in Los Angeles photochemical smog by Prof. Arie Haagen-Smit and others was driven in part by a critical need to understand the effect of the air pollution on plants and ecosystems in the area (*5*). Extreme air pollution episodes leading to health issues and damage to vegetation have prompted the adoption of strict air pollution regulations in many countries. For example, the United States established the National Ambient Air Quality Standards (NAAQS), under authority of the Clean Air Act; these standards have resulted in dramatic improvements in the air quality in many regions across the country (*6*). Improved air quality has led to massively positive effects on the economy due to the reduction in the number of air pollution-related hospital visits, reduction in the number of days missed from school and work, and improved crop production. In terms of the impact on the economy, the benefits of the Clean Air Act have exceeded the cost by a wide margin making it one of the most successful pieces of legislation passed in the United States in the 20th century (*7*).

Despite the impressive progress over the years, the air pollution problem is far from being solved. The State of Global Air 2018 gives a comprehensive overview of air quality and health levels as well as trends since 1990 (*8*). According to the report, air pollution is the fourth leading risk factor for mortality globally. Millions of people still die each year from diseases associated with their exposure to air pollution and even more suffer from a range of short- and long-term health effects from the development of asthma to a decrease in cognitive function. Airborne particles, or particulate matter, represent an especially potent agent of the adverse health effects of polluted air. The particles with an aerodynamic diameter below

2.5 μm ($PM_{2.5}$) were the sixth-ranking mortality risk factor in 2015, with exposure to $PM_{2.5}$ accounting for 4.1 million deaths that year (*8*).

Global and regional climate patterns are also directly affected by air pollutants. The warming effect of greenhouse gases on the climate is well known, and is relatively easy to describe in quantitative terms. Particles have a more uncertain and poorly understood effect on the climate because of their ability to absorb and scatter solar radiation and modify properties of clouds in a very complex way (*9*). Part of the challenge in accurately modeling the climate effects of particles is the impressive amount of diversity in their chemical and physical properties. For example, soot particles absorb sunlight very strongly (*10*) but are poor cloud nuclei because of their hydrophobicity. In contrast, particles dominated by ammonium sulfate, a major $PM_{2.5}$ constituent in urban areas, do not absorb sunlight and are highly hygroscopic. Biomass burning smoke occupies a position in between these two extremes as it contains light-absorbing "brown carbon" constituents (*11*, *12*), which have a range of hygroscopic properties.

Another challenge for predicting climate and health effects of air pollutants is the highly dynamic nature of the atmospheric environment. The composition of the atmosphere at any given time and at any given place can be described by the species present, their concentrations in different phases, and their physical and chemical properties. The atmospheric composition is largely determined by what is emitted by people and nature and by the complex motion of the atmospheric masses. However, it also depends on how fast species are removed from the atmosphere and transform to yield new products through a combination of chemical and physical processes, involving multiple phases. These "aging processes" occur on local scales as air masses travel across a city and on a global scale as they travel around the globe. These transformations result in the formation of additional gas-phase species, and new particles, as well as in the removal of both gases and particles by precipitation (wet deposition) or by Earth surfaces (dry deposition). Chemical aging processes for particles include reactive uptake of gas-phase oxidants (*13*), coupled gas-particle partitioning and oxidation (*14*), and surface and condensed-phase photochemical processes driven by sunlight (*15*). The aging processes involve multiple phases, and they are excellent examples of the multiphase chemistry described in this book.

Previous improvements in air quality in the United States and in many developed countries have been made possible by the advancement of our fundamental knowledge of gas-phase chemistry that came from extensive laboratory experiments on photooxidation of hydrocarbons (*3*). Our ability to understand the air pollution system and predict how it responds to various chemical and physical perturbations, such as an increase in the emission of a particular class of compounds or increase in global temperature, has enabled the implementation of effective strategies to reduce the concentration of air pollutants. However, gas-phase chemistry alone cannot encompass the full complexity of atmospheric processes – a famous example of this is the dramatic failure of gas-phase mechanisms to predict the existence of the ozone hole over the Antarctic. This phenomenon could only be described by including the efficient releases of photochemically active chlorine from its more abundant and less active condensed-phase reservoir species (*16*). As improvements in

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understanding have been achieved, the problem has become more challenging. Through further advancements in scientific knowledge of the composition and multiphase chemistry of the atmosphere, we will be better prepared for the future, and be able to more effectively plan the economic developments to ensure that all people have access to clean air (Figure 1).

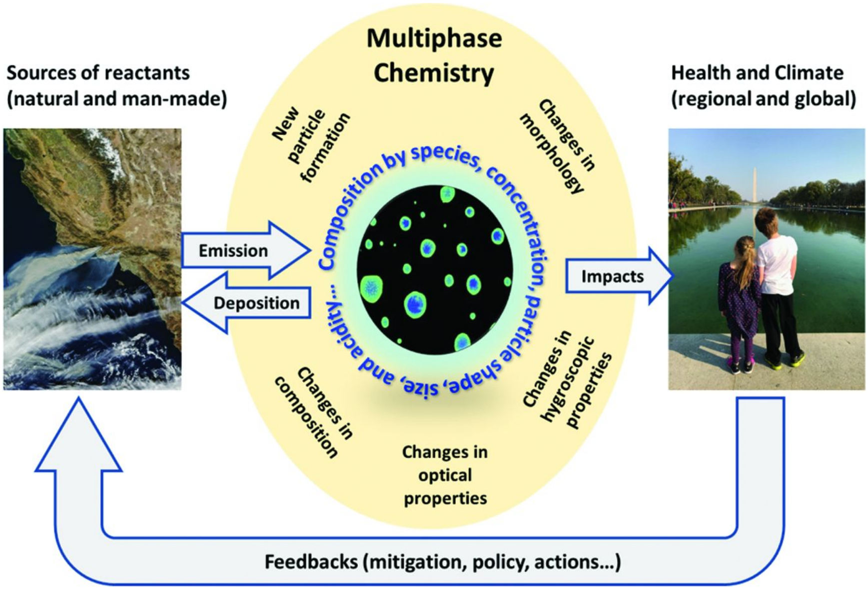

Figure 1. Multiphase chemistry changes the chemical nature and physical properties of the compounds emitted by natural and anthropogenic sources. The air pollutants aged by multiphase processes affect both humans and ecosystems, which in turn affects the emission and deposition of additional air pollutants. Understanding multiphase chemistry is critical for assessing the local and global effects of air pollutants. The image on the left is credited to NASA, and image on the right was taken by one of the authors. The image in the middle is a false colored SEM image illustrating extent of the multi-phase variability in individual atmospheric particles, where green and blue colors depict their organic and inorganic components, respectively.

At any given time, the composition of the atmosphere affects the health of people and the environment, as well as the entire climate system. These impacts can be assessed with a variety of metrics. Mortality and morbidity are the usual metrics for health effects in people, while the health of the environment may be measured by impacts on weather and climate, clouds and precipitation, the amount of light that reaches the Earth's surface, and the diversity and vitality of ecosystems. Understanding the atmospheric composition and how it might respond to changes in emissions, climate, or deposition enables the development of useful models and practical solutions for improving the air quality. While the models and measurement tools are now more complex, the overall goal and process remain to understand what is in the air and how it will respond to environmental changes. With improved fundamental knowledge, scientists can inform decision-makers on a range of issues, from impacts of individual actions to new policies regarding emissions, city development, or energy production.

With a goal of introducing some of the most recent advances in multiphase chemistry and its importance in the atmosphere, the chapters in this book are organized according to several themes. The first section focuses on recently discovered chemical reactions and processes. These include understanding several intermediates and pathways that were not considered in the early air quality studies. Several important physical characteristics of aerosols are described in the second section. These characteristics may impact the chemical reactions that take place within the aerosols or on their surfaces. They also elucidate how solar radiation may interact with aerosol particles. The third section includes two chapters highlighting recent model advances that begin to incorporate multiphase processes. The final two sections shift focus to two topics that are currently receiving a great deal of attention. Three chapters focus on the characterization of emissions from fires and the multiphase chemistry that occurs as these emissions move through the atmosphere. Finally, the last section includes chapters that describe the use of new techniques developed to understand the strength of potential health impacts or toxicity of particles based on a measure of their oxidative potential - this indicates their ability to produce oxidation reactions, which have negative impacts in the body.

None of the topics are covered exhaustively in this collection, but rather each is introduced along with recent findings and references to additional work. By presenting these topics together, additional connections can be identified across them, leading to even more multidisciplinary multiphase chemistry knowledge.

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