

# Atmospheric Chemistry

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The field of atmospheric chemistry is very broad, both in the problems addressed and in the approaches taken. Thus, it includes laboratory and theoretical studies, field measurements, and modeling, and addresses chemistry from the lower to the upper atmosphere, in remote and polluted regions, from marine to continental areas, and both outdoors and indoors. Given this complexity, it is impossible to capture all aspects with the limited number of articles that can be included in a special feature. Thus, what follows should be taken as illustrative rather than inclusive.

The genesis of the field of atmospheric chemistry lies in air pollution in the troposphere (lower atmosphere), for which there is documentation at least as long ago as the 13th century. Dramatic incidents of excess deaths such as in the Meuse Valley, Belgium, in 1930 (1), and in London, England, in 1952 (2) brought public and scientific attention to “smog” (smog = smoke + fog) and, in particular, to the problem of sulfur dioxide and sulfate particles it forms in air, as well as to direct emissions of particles from combustion sources. Around 1950, what initially appeared to be a different kind of smog, now known as photochemical air pollution, was recognized in the Los Angeles area. The seminal work of Haagen-Smit demonstrated that the necessary ingredients (primary pollutants) were volatile organic compounds (VOC), oxides of nitrogen ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), and sunlight. The wavelengths available to drive photochemistry at the earth’s surface are restricted to  $\lambda > 290 \text{ nm}$  due to the filtering of shorter wavelengths by ozone naturally produced in the stratosphere (upper atmosphere) via the Chapman Cycle (3). The photochemistry of VOC with  $\text{NO}_x$  was shown to generate ozone and a host of additional “secondary” pollutants, including nitric acid, peroxyacetyl nitrate, and particles containing nitrate, sulfate, and organics. It took a number of decades to sort out the essentials of the gas phase chemistry that was involved; indeed, it was not until 1970 that the hydroxyl radical was recognized as being a key driver of chemistry throughout the atmosphere (3). Since then, the role of ozone, the nitrate radical, and halogen atoms have also become evident (3, 4). Elucidation of the fundamental chemistry of photochemical air pollution, and subsequently of acid deposition, revealed that the  $\text{SO}_2$ -associated smog was driven

by the same intermediates and processes, rather than being a separate phenomenon.

In the 1970s, scientific interest in atmospheric chemistry expanded with the recognition of the close linkage between the chemistry of the troposphere and the stratosphere. For example, it is only species of little or no reactivity in the troposphere—such as the chlorofluorocarbons used as aerosol propellants, blowing agents, and refrigerants—that have sufficiently long lifetimes to reach the stratosphere. At these altitudes, they are exposed to shorter wavelengths at which they photolyze, leading to destruction of ozone (5). The 1995 Nobel Prize in Chemistry was awarded to Crutzen, Molina, and Rowland for their work on stratospheric ozone chemistry and discovery of new ozone destruction mechanisms associated with anthropogenic emissions (5, 6).

The discovery of the dramatic loss of ozone in the Antarctic “ozone hole” in the mid- 1980s and the discrepancy between measurements and predictions using models having only gas phase chemistry brought to the fore the need to understand so-called “heterogeneous chemistry”—i.e., chemistry between gases and species on or in condensed phases. Although such multiphase chemistry had been suggested before this to be of importance in the lower atmosphere, experiments on such systems were plagued by the difficulty of carrying out studies under well controlled conditions with well defined surfaces at one atmosphere pressure in air at ambient temperatures and in the presence of water vapor. So, although it is now clear that heterogeneous chemistry and photochemistry play a key role in tropospheric chemistry, both outdoors and indoors, understanding these processes on a molecular level remains in most cases quite challenging.

A closely related area is the formation, growth, and fate of particles in air due to gas-to-particle conversion, and condensed phase reactions that occur in particles. This is particularly complex for organic reactions where the secondary organic aerosol (SOA) formed likely consists of hundreds, if not thousands, of individual compounds including polymers. Continuous exchange between the condensed and gas phases, which appears to depend on a number of factors including temperature, relative humidity, and available sunlight, combined with oxidation in both phases by a number of species such as OH,  $\text{O}_3$ ,  $\text{NO}_3$ , and halogens,

further complicates the full understanding of airborne particles and their impacts.

Although the potential climate impacts of fossil fuel combustion were highlighted by the historic  $\text{CO}_2$  records of Keeling (7), there was initially little emphasis on the coupling between this phenomenon and air pollution. However, over the last several decades, the interweaving of climate and air pollution and their relationship to fossil fuel usage and combustion has become widely accepted. Thus, ozone, chlorofluorocarbons, methane, and nitrous oxide are all significant greenhouse gases and, indeed, their contribution in sum to radiative forcing is similar to that of  $\text{CO}_2$  (8). Another important coupling involves particles either directly emitted from fossil fuel combustion (e.g., soot) or those formed in air from reactions of primary pollutants (9). Such particles have been shown to have significant effects on human health and visibility (10). Because they scatter sunlight (hence degrading visibility), they also have a direct effect on climate. Furthermore, they affect the formation and properties of clouds, including their lifetimes, causing indirect climate impacts. Understanding and prediction of the role of particles represents the largest uncertainty today in estimates of the impact of anthropogenic activities on climate (8); hence, this is one of the most active areas of current research in atmospheric chemistry. It is clearly critical for the development of integrated control strategies that effectively address all aspects of anthropogenic perturbations on the atmosphere that their interconnectedness be recognized and understood both qualitatively and quantitatively (11, 12).

The complexity of the atmospheric system is such that laboratory and theoretical studies, field campaigns, and computer kinetics studies must all be brought to bear. Indeed, one of the hallmarks of recent advances in atmospheric chemistry is full integration of these approaches, without which some important pieces of the puzzle are often missing. Thus, theory informs experiments and vice versa to provide molecular-level insights that would not otherwise be possible. Similarly, intercomparison of results from laboratory, field, and model studies has in

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some cases revealed inconsistencies in our understanding of important chemistry and highlighted important gaps in our knowledge.

In summary, the chemistry occurring in the atmosphere—from remote to polluted urban regions, from marine to continental regions, from the lower to the upper atmosphere, and indoors as well

as outdoors—is all closely coupled. Indeed, it is most faithful to the science to regard them all as points on a continuum connecting emissions through chemistry and transport, and ultimately, to the impacts on human health and welfare. The articles in this special feature of necessity only scratch the surface of this field. However, it is

hoped that they will serve to illustrate the breadth of the problems and approaches taken, and to encourage researchers from other areas to bring their talents and expertise to bear on the critical and challenging issues in atmospheric chemistry that have such important societal implications.

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