Atmospheric chemistry, aerosols, and climate: global coupling

John H. Seinfeld
Division of Engineering and Applied Science and Department of Chemical Engineering
California Institute of Technology, Mail Code 104-44
Pasadena, CA 91125
seinfeld@caltech.edu

Abstract

The chemistry of the atmosphere occurs within a fabric of profoundly complicated atmospheric dynamics, and the life cycles of the chemical constituents of the atmosphere are linked together in complex ways. A perturbation in one component can lead to significant, and nonlinear, changes in other components and to feedbacks that can amplify or damp the original perturbation. The atmospheric increase of greenhouse gases over the past century is predicted to lead to a warming of the Earth that will produce changes in the basic chemistry of the atmosphere that, themselves, will feed back to affect the temperature increase, itself. Recently scientists have begun to assess how increasing anthropogenic aerosols affect global climate. Aerosols can produce both cooling and heating; on the whole, evidence suggests aerosols cause cooling, but it is not known confidently just how large such an effect might be. Aerosol concentrations depend, in part, on the gas-phase chemistry of the atmosphere that serves to convert species from the gas to the particle phase. Analyses of the effect of changing trace gas and aerosol levels on climate must account for the coupling and feedbacks that occur in the chemistry-aerosol-climate system. A framework for these couplings is described, with several examples presented.
1 Introduction

Human activities are leading to changes in the composition of the atmosphere. These changes occur directly through emissions of trace gases and aerosols and also through perturbations in the biosphere itself, which influence the rates of production and removal of atmospheric constituents.

Direct emissions to the atmosphere as a result of anthropogenic activities include such well-established compounds as CO$_2$, SO$_2$, and NO$_x$ from fossil fuel combustion and chloroflourocarbons from consumer uses. In these cases emissions estimates are relatively accurate because of the link to major industrial activities. In many other situations involving direct emission of trace gases and aerosols it is much more difficult to obtain accurate emissions estimates. A prime example of such a situation is biomass burning, which occurs annually over wide areas in the tropics and is estimated to release large quantities of trace gases and aerosols into the atmosphere. Anthropogenically-influenced changes in the Earth's system can also lead to atmospheric emissions. As land use and agricultural practices change, emissions of trace gases such as CH$_4$, N$_2$O, and NO change in response. How much these emissions change as a result is often difficult to assess.

Once released into the atmosphere, virtually all trace gases and aerosols are subject to chemical transformation. This transformation occurs over a spectrum of spatial and temporal scales that range from a few meters to the entire globe and from the order of seconds to a century or more. As atmospheric levels of some trace species change, the actual chemical functioning of the atmosphere is affected. In turn, the production and removal rates, and hence lifetimes, of other species are indirectly affected. Also, directly emitted substances may be transformed chemically into a product that is much more climatically active than its parent compound. Sulfur dioxide, for example, is converted to sulfate aerosol, which exerts an important radiative forcing effect. The actual amount of sulfate aerosol produced depends on a complex interplay of atmospheric transport, gas-phase oxidative capacity, and interactions with other substances in the aerosol phase.

2 Chemistry-Climate Coupling

In many instances feedback loops develop, where a change in one variable induces changes in other variables that, in turn, cycle back to affect the original variable. As the Earth's radiative balance is altered as result of changes in trace gas and aerosol emissions, atmospheric circulation patterns change, detailed aspects of the water cycle change, such as water availability at the surface and the water vapor content of the atmosphere, all of which act to modify the atmospheric budgets of the trace gases and aerosols that initiated the process of change in the first place.

Methane, the second most important greenhouse gas after CO$_2$, illustrates some of the complexity surrounding prediction of future trends.
sources such as rice paddies and cattle are increasing, and are relatively easy to assess. Methane is removed from the atmosphere by reaction with the hydroxyl radical, OH. The concentration of OH depends generally on the amount of CO in the atmosphere; CO is itself another trace gas with significant sources from fossil fuel use and biomass burning, and hence its global level is changing. Global OH depends also on the ozone column, and the local amount of ozone and NO\textsubscript{x}, all of which are affected by human activity. Changes in CH\textsubscript{4} can affect the amount of ozone and OH, and changes in OH can affect tropospheric concentrations of halocarbons, also greenhouse gases. Furthermore, effects of ozone on climate may feed back on sources and sinks of CH\textsubscript{4} through temperature changes.

3. Aerosols

Figure 1 depicts several aspects of chemistry/aerosol/climate coupling. Climate effects are represented in terms of radiative forcing, a perturbation of the Earth’s radiative balance, expressed as W m\textsuperscript{-2}. Fueled by anthropogenic and biogenic emissions of trace gases and stratospheric inputs of O\textsubscript{3}, the gas-phase chemistry of the troposphere generates O\textsubscript{3}, as its principal long-lived product. Tropospheric ozone, itself, is a greenhouse gas and contributes to radiative forcing. The signature species of tropospheric chemistry is the hydroxyl (OH) radical, which fuels virtually all tropospheric reactions of importance. The hydroxyl radical level governs, for example, the generation of inorganic (sulfate and nitrate) and organic aerosols by gas-to-particle conversion and nucleation and thus serves to couple gas-phase chemistry and tropospheric aerosols. Figure 2 shows how increased emissions of VOC/NO\textsubscript{x} and aerosols can affect the climate system.

Aerosols occur naturally in the troposphere from sources such as sea salt, mineral dust, fires, and sulfate aerosol formation from biospheric emissions. As the only basic gas of importance in the atmosphere, ammonia (NH\textsubscript{3}) is ubiquitous; it readily combines with acidic aerosol species to produce aerosol ammonium (NH\textsubscript{4}\textsuperscript{+}) compounds. If the atmosphere were devoid of aerosols, the Earth would be devoid of clouds; aerosols are the cloud condensation nuclei (CCN) around which cloud droplets form. More often than not, clouds evaporate rather than precipitate, returning the cloud condensation nuclei back to the atmosphere. The arrow in Figure 1 depicting this evaporation process is labeled, “Cloud processing”, since the particles returned to the atmosphere upon evaporation may be chemically different from the original CCN if aqueous-phase chemical processes occurred in the cloud droplets while they were present. The most notable process in this regard is the aqueous-phase formation of sulfate (SO\textsubscript{4}\textsuperscript{2-}) from the oxidation of SO\textsubscript{2} that dissolved in the cloud water.
Chemistry / Aerosol / Climate Coupling

Radiative Forcing

Anthropogenic
Biogenic
Tropospheric O₃
Stratospheric input

Gas-phase Tropospheric Chemistry

Heterogeneous NOₓ/ NOᵧ chemistry
Free radical scavenging?
Alteration of actinic flux

Tropospheric Aerosols

Sea salt
Mineral dust
Biomass burning particles
Sulfates (via gas-phase chemistry)
Carbonaceous particles

Direct effect

Flux of gaseous species to clouds

Cloud processing

CCN

Alteration of cloud albedo (indirect effect)

Cirrus
Stratus

Figure 1.
Increased Tropospheric Temperatures

Increased VOC Emissions

Increased 
H₂O Vapor

Upper Tropospheric O₃
(+)

Increased Tropospheric Temperatures

Increased VOC Emissions

Increased H₂O Vapor

Decreased Transport of CFCs to Stratosphere

Decreased UV Solar Radiation to Troposphere

Increased Tropospheric Oxidation

Tropospheric Oxidants
(+ or ?)

Tropospheric Oxidants
(+)

Tropospheric Oxidants
(+ or ?)

Tropospheric Oxidants
(+)

Increased Emissions of Aerosols and Aerosol Precursors (e.g. SO₂)

Increased Tropospheric Actinic Flux (scattering aerosols)

DeCREASED ActINIC Flux (absorbing aerosols)

Tropospheric Aerosols
(+)

Increased VOC / NOₓ Emissions

Figure 2.
References


