Chapter 1

Introduction

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1.1 Background and Motivation

Atmospheric aerosols (airborne particulate matter) have significant impacts on climate, visibility, and human health and aerosol composition is critically important for all of these impacts. Composition is relevant to human health because the chemistry of a particle determines its toxicity. Visibility is affected because composition controls hygroscopicity, which determines the size and optical properties of a particle. Aerosols affect climate in two principal ways: 1) directly, by scattering and absorbing incoming solar radiation and 2) indirectly, by affecting the radiative properties and lifetime of clouds. Composition influences the direct effect for the same reasons that it impacts visibility, while its role in the indirect effect stems from the fact that the ability of an aerosol to act as a cloud condensation nuclei (CCN) is determined by both its size and chemical makeup. Figure 1.1, from the 2007 International Panel on Climate Change assessment report, shows that the magnitude of the cooling from direct and indirect effects of aerosols may equal or exceed the warming generated by greenhouse gases. Perhaps more importantly, the uncertainty in the magnitude of the direct and indirect radiative effects of aerosols dwarfs the uncertainty associated with warming caused by greenhouse gases (IPCC, 2007).

Aerosols can be emitted directly from a source or they can form in the atmosphere when gas-phase precursors are reacted and become nonvolatile enough to condense. These two mechanisms are known as primary and secondary aerosol formation respectively. There are anthropogenic and biogenic sources of both primary and secondary aerosol. While the inorganic composition of atmospheric aerosols has been studied for many years, only recently has the development of new instrumentation allowed for quantitative measurement of the organic fraction of atmospheric aerosol. It is now understood that organic aerosols represent a significant fraction of the submicron aerosol mass throughout the world (Zhang et al., 2007), and that a large fraction of the organic aerosol is secondary. While results from a wide variety of instruments are presented in this thesis, particular emphasis is given to results obtained using an Aerodyne compact Time of Flight Aerosol Mass Spectrometer (C-ToF-AMS). The development of this online aerosol mass spectrometer has provided increased sensitivity and time-resolution necessary to make quantitative airborne measurements of ambient organic aerosol both at low loadings and in highly concentrated, but spatially narrow plumes emanating from point sources. To obtain the results presented in this thesis, it was necessary to carry out the first-ever airborne deployment of a C-ToF-AMS instrument.

1.2 Organization of Thesis

This thesis presents results on the sources and impacts of atmospherically relevant aerosol, particularly organic aerosol. Emphasis is placed on the use of compositional measurements as a tool to determine the sources of atmospheric aerosol, the mechanisms by which it is formed, and the impact of aerosol on human health and climate. Chapters 2 and 3 describe laboratory-based experiments in large (22 m^3) environmental chambers. These experiments explore the mechanisms that allow gas-phase compounds, specifically isoprene and amines, which were previously thought too volatile to condense, to form aerosol. Chapters 4 and 5 describe airborne field experiments where the physical and chemical characteristics of aerosol from globally and regionally important sources are quantified. Relationships between the aerosol observed during the field and chamber studies are also discussed. The final chapter summarizes the results of the previous chapters and presents areas of ongoing research at the frontiers of aerosol-cloud interactions.

Chapter 2 presents a detailed analysis of the chemical composition of aerosol formed from the oxidation of isoprene. Isoprene has long been known to be the most abundant gas-phase volatile organic compound (VOC) on Earth, but until recently it was not thought to contribute to aerosol formation because the products of its gas-phase oxidation were too volatile (Appendix A gives details on the aerosol yield from isoprene). Chapter 2 demonstrates that the majority of aerosol formed from isoprene photooxidation under high-NO_x conditions is derived from further oxidation of the first generation product methacrolein. The significant differences in the chemical composition of aerosol formed under high and low-NO_x conditions are explored and the importance of oligomers and peroxides is discussed. Comparisons between online and offline mass spectroscopic techniques are used to confirm that the observed aerosol-phase products are not artifacts.

The potential for alkylamines to form aerosol is explored in Chapter 3 through a series of laboratory chamber experiments and thermodynamic calculations. Aerosol formation from reaction of amines with OH, ozone, and nitric acid is investigated and aminium nitrate salt formation is found to be a dominant aerosol formation pathway. Significant non-salt organic aerosol is also observed during the oxidation of certain amine precursors. Thermodynamic calculations show that a small subset of the amines studied is capable of forming aminium nitrate salts under atmospheric conditions where the gas-phase ammonia concentrations are typically significantly higher than those of amines.

Chapter 4 presents results from flights near a major bovine source in the San Joaquin Valley of California. Agricultural emissions are a significant source of particulate pollution and this study characterizes the chemical and physical characteristics of aerosol emitted from this globally important source. The mass of aminium nitrate species, observed in the chamber experiments of Chapter 3, is also quantified. The sub- and supersaturated water uptake behavior of aerosol from the source is described and a relationship between these two regimes of hygroscopic growth is found.

Aerosol emissions from a modern container ship are described in Chapter 5. The study presented represents the first-ever simultaneous shipboard and airborne measurements of container ship emissions. Particulate emissions from the ship are found to contain significantly more organic than estimated from previous field campaigns. This additional organic mass is found to impact global emission factors of organic particulates from shipping and the activity of ship emissions as cloud condensation nuclei .

Chapter 6 summarizes the results of the thesis and describes current research efforts at the frontier of aerosol-cloud interaction. The current research efforts focus on the potential of reactions within cloud droplets to form organic aerosol and the impact of chemical composition on the ability of aerosol to act as ice crystal nuclei (IN).

Appendix A gives details on the aerosol yields from the photooxidation of isoprene under a wide range of conditions. Appendix B presents a thorough analysis of the nature of organic aerosol in the Los Angeles Region. Appendix C presents a comparison of theoretically predicted (based on compositional inputs) and measured hygroscopic particle growth in a marine environment.

1.3 References

1. Intergovernmental Panel on Climate Change (IPCC) (2007). Climate Change 2007, Cambridge, UK: Cambridge Univ. Press, Cambridge and New York.

2. Zhang, Q., J.L. Jimenez, et al., “Ubiquity and Dominance of Oxygenated Species in Organic Aerosols in Anthropogenically—Influenced Northern Hemisphere Mid-latitudes” *Geophysical Research Letters*, 34, L13801, 2007.

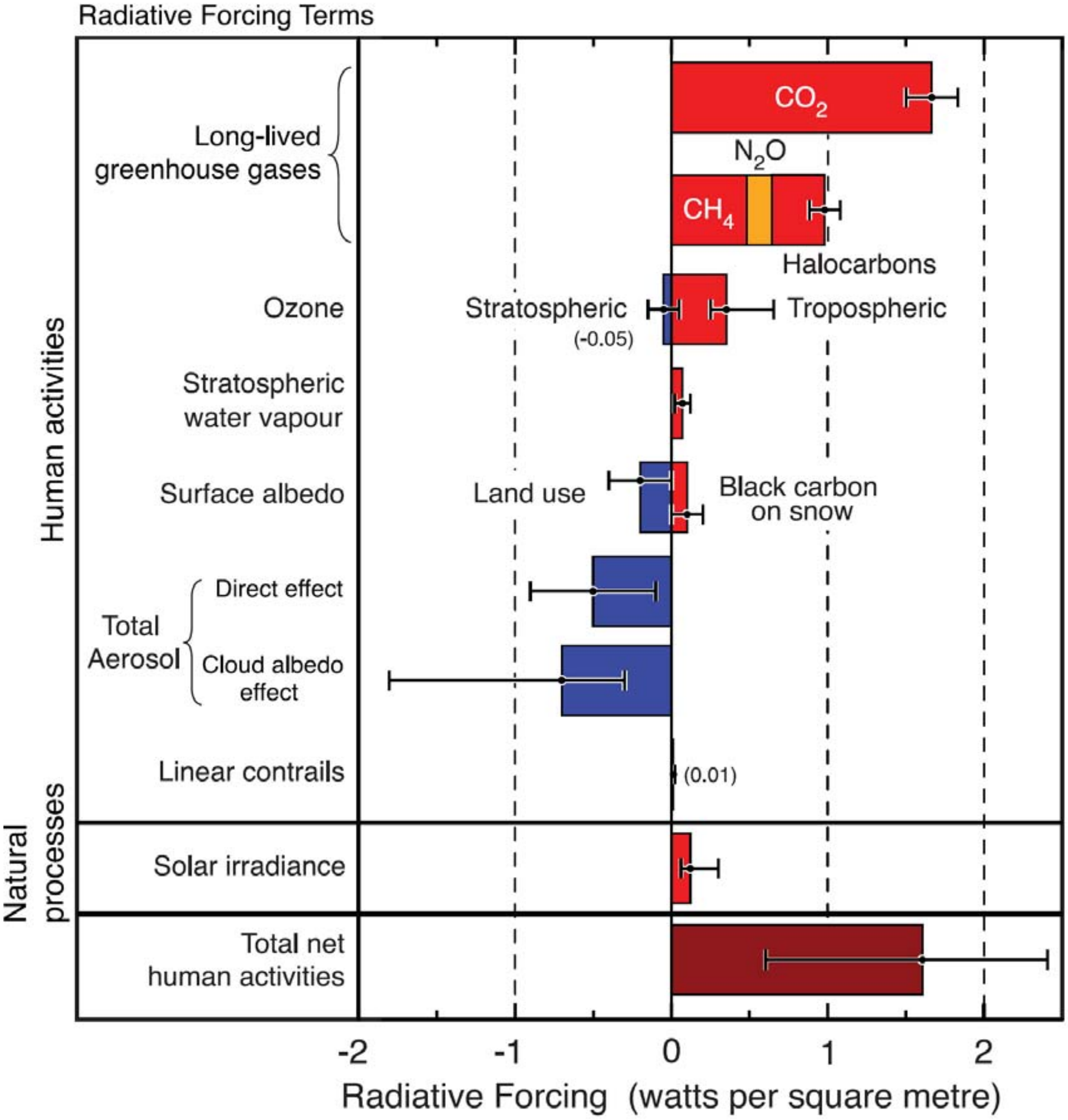

Figure 1.1: Estimated radiative forcing of climate in 2005 relative to pre-industrial times.