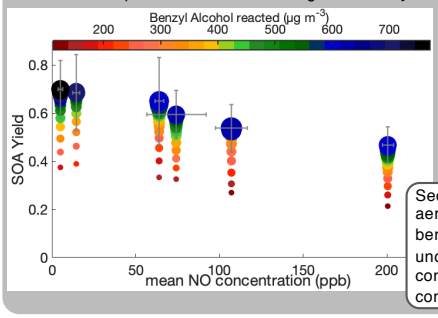
JOHN SEINFELD LABORATORY

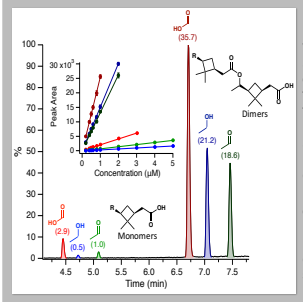
Chamber Studies

Recent inventory-based analysis suggests that emissions of volatile chemical products in urban areas have become competitive with those from the transportation sector, as emissions from motor vehicles have declined. Understanding the potential for secondary organic aerosol formation from these volatile chemical products is, therefore, critical to predicting levels of aerosol and for formulating policy to reduce aerosol exposure. Experimental and computationally simulated environmental chamber data provide an understanding of aerosol yield and chemistry under relevant urban conditions and give insight into the effect of volatile chemical products on the production of secondary organic aerosol.



Secondary organic aerosol yield of benzyl alcohol under different constant nitric oxide concentrations

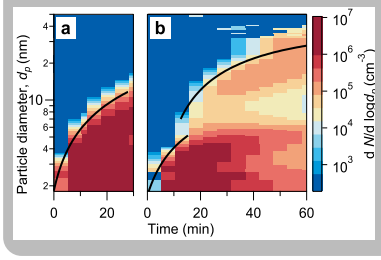
Instrument Sensitivity



Monoterpenes ($C_{10}H_{16}$), emitted in large quantities from terrestrial vegetation (~150 Tg y^{-1}), represent a dominant source of secondary organic aerosol globally. Deciphering the molecular composition, and in turn formation mechanisms, of monoterpene secondary organic aerosol is essential to reducing uncertainty in assessment of its environmental and health impacts. However, molecular characterization of monoterpene SOA is significantly hindered by its chemical complexity. Liquid chromatography/negative electrospray ionization mass spectrometry [LC/(–)ESI-MS] is routinely employed to characterize the identity and abundance of molecular products in SOA derived from monoterpene oxidation. Due to a lack of authentic standards, however, commercial terpenoic acids are typically used as surrogates to quantify both monomeric and dimeric SOA constituents. Here, we synthesize a series of enantiopure, pinene-derived carboxylic acid and dimer ester homologues. We find that the (–)ESI efficiencies of the dimer esters are 19 to 36 times higher than that of *cis*-pinonic acid, demonstrating that the mass contribution of dimers to monoterpene SOA has been significantly overestimated in past studies. This demonstrates that the use of unrepresentative surrogates can lead to substantial systematic errors in quantitative LC/ESI-MS analyses of SOA.

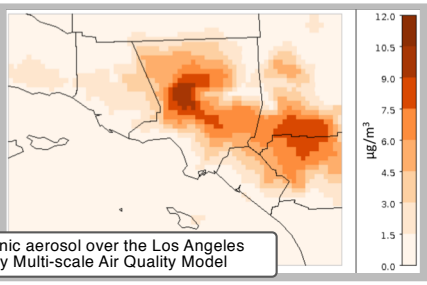
Nucleation Studies

The formation of nanometer-sized atmospheric particles from reactive gases and their subsequent growth contribute to half of the cloud droplets concentration globally and is often observed in cities forming visible particulate pollution. In order to better characterize and understand nanoparticle formation and early growth, we performed a number of experiments under various atmospheric conditions in the Cosmics Leaving OUtdoor Droplets (CLOUD) chamber at the European Organization for Nuclear Research (CERN). The CLOUD chamber and CERN facility allow us to measure particle nucleation and growth from a precisely well-controlled mixture of organic and inorganic vapors without interference with particulate or gaseous contamination. With the help of Caltech-designed particle sizing instrument, we have found that simultaneous condensation of nitric acid and ammonia vapors to tiny particles, as small as 2 nanometers in diameter, can cause them to grow very rapidly. This recently-found mechanism is likely to explain how freshly nucleated particles can survive through the smallest size range where they are most vulnerable to scavenging loss, thus greatly increasing their survival probability in megacities.



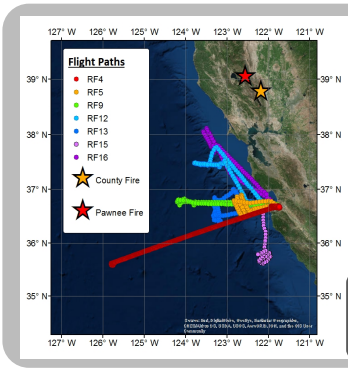
Regional Modeling

Atmospheric modeling efforts now address the global effect of aerosols on climate, the coupling between atmospheric chemistry, aerosols, and climate, and the microphysics of aerosol-cloud interactions. A major goal of much of the work worldwide in global aerosol modeling is to narrow the uncertainties in predicting the effects of aerosols on climate. Physical and chemical representations of the aerosol-related processes are developed on the basis of detailed microscale models, or laboratory data, and implemented in large-scale models.



Simulated secondary organic aerosol over the Los Angeles Basin using the Community Multi-scale Air Quality Model

Field Studies



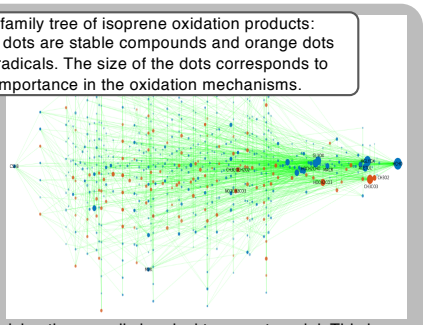
Because of the complexity of aerosol-cloud interactions, observations of clouds provide essential information to evaluate models of cloud formation and evolution in atmospheric models. For example, aerosol-induced changes in the number and size distribution of cloud droplets affect the development of precipitation, the amount of precipitation that actually reaches the ground, and the persistence of precipitation. One effect of this is that clouds may persist longer and increase in spatial coverage. Our group has utilized the Navy Twin Otter aircraft, located in a large, fully-equipped hangar at the Marina Municipal Airport, a few miles north of Monterey, CA.

Trajectories of seven research flights from the MACAWS campaign. Colored stars indicate the locations of the County and Pawnee Fires, which led to occasional sampling of biomass burning plumes.

Machine Learning

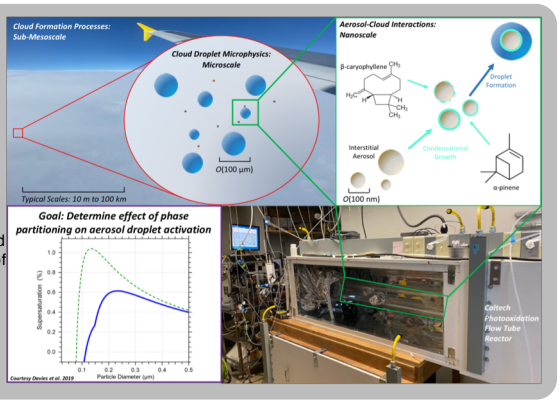
The temporal evolution of species emitted to or formed in the atmosphere is evaluated by three-dimensional chemical transport models simulating simultaneous chemical reactions and transport. The number of all the species comprising atmospheric chemistry can be immense. For example, atmospheric oxidation isoprene alone involves 1926 individual reactions and generates 587 new species. Moreover, representing the detailed steps that proceed from initial oxidation of a volatile organic compound with the principal oxidants, OH, O_3, or NO_3, to important products is a major challenge in atmospheric chemistry. Generally, chemical mechanisms employed in atmospheric models are limited to a few hundred species and reactions, which still can require up to 90% of the overall computational resources for solving the overall chemical transport model. This is a severe limitation to the ability to simulate atmospheric chemistry. We develop and verify the performance of machine learning algorithms to represent highly explicit atmospheric chemistry and aerosol formation in atmospheric models.

The family tree of isoprene oxidation products: blue dots are stable compounds and orange dots are radicals. The size of the dots corresponds to the importance in the oxidation mechanisms.

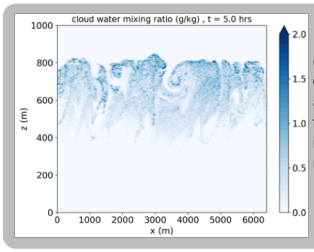


Cloud Droplets

In the atmosphere, cloud droplets form on aerosol particles, commonly known as cloud condensation nuclei (CCN). The ability of an aerosol to serve as a CCN is influenced heavily by its chemical composition, though there is still much debate over which physicochemical properties of aerosols most significantly contribute to an aerosol's CCN ability. Recently, it has been suggested that the surface tension of the activated aerosol (and the resulting cloud droplet) plays a much larger role than previously thought, and this project aims to determine the influence of the phase partitioning of inorganic and organic constituents in aerosol particles onto its surface tension. The goal is to better quantify which aerosols may serve as CCN and further describe how the interactions between gases and particles (many of which are anthropogenically-derived) influence climate.



Cloud Simulations



Clouds are a critical component of the climate system because of their effects on radiation and precipitation. But clouds would not exist on Earth without aerosols. How large those droplets become determines how much radiation that cloud will reflect and how much it will rain. We simulate the aerosol-cloud interactions and cloud dynamics using a Lagrangian cloud model. This allows us to study complex and usually unresolved cloud processes.

Cloud water mixing ratio (g/kg) in a 2D simulated stratocumulus cloud from the DYCOMS-II RF02 LES case.

Members

John Seinfeld (seinfeld@caltech.edu)
Reina Buenconsejo (rbuencon@caltech.edu), Chemistry, G2 (co- with Wennberg)
Sophia Charan (scharan@caltech.edu), Chem Engineering, G4
Yuanlong Huang (yhuang@caltech.edu), Environ Sci & Engineering, Postdoc
Christopher Kenseth (ckenseth@caltech.edu), Chemistry, G5 (co- with Wennberg)
Stephanie Kong (wkong@caltech.edu), Chem Engineering, G5 (co- with Flagan)
Elyse Pennington (epenning@caltech.edu), Chem Engineering, G3
Brigitte Rooney (brooney@caltech.edu), Environ Sci & Engineering, G5
Ben Schulze (bschulze@caltech.edu), Environ Sci & Engineering, G2
Clare Singer (csinger@caltech.edu), Environ Sci & Engineering, G2 (co- with Schneider)
Ryan Ward (rxward@caltech.edu), Environ Sci & Engineering, G1

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