Oxidation Chemistry and Secondary Organic Aerosol Formation in Indoor and Outdoor Atmospheres

Nadia Tahsini

ABSTRACT

Particulate matter exerts a significant influence on climate and air quality, including harmful human health impacts. A substantial fraction of particulates are aerosols, comprised largely of secondary organic aerosol (SOA) formed from photochemical reactions of volatile organic compounds (VOCs). SOA formation occurs across scales, ranging from the outdoor atmosphere to indoor environments, and improved understanding of this chemistry is required to more accurately quantify impacts on climate and human health. This thesis investigates oxidation chemistry and SOA formation in indoor and outdoor atmospheres, including a focus on peroxy radical (RO_2) chemistry.

In the first part of this work, we examine the oxidation of isoprene, an atmospherically abundant biogenic VOC. Most global models currently use SOA yields for isoprene that assume NO_x linearity, limiting the accuracy under intermediate conditions. Using environmental chamber experiments, we characterize the product distributions and SOA formation from isoprene oxidation under the full atmospheric range of RO_2 regimes. We provide yields for major gas-phase species and aerosol as a function of key RO_2 parameters, highlighting the non-linear NO_x dependence of SOA contrary to traditional assumptions, which can be used to improve the treatment of isoprene SOA in climate models.

The second part of this work investigates how chemistry and volatility interplay for the temperature dependence of SOA formation, focusing on the ozonolysis of α-pinene, another prominent biogenic VOC emitted into the atmosphere. While SOA formation has been shown to be temperature dependent based on volatility effects, the temperature effect of chemistry - especially RO_2 isomerization - is less explored. With environmental chamber experiments and box modeling, we examine how chemistry versus volatility effects impact the overall temperature dependence of SOA, using speciated gas-phase measurements and aerosol-phase analysis. This work provides novel insight on how chemistry and volatility contribute to SOA formation across temperatures, including a focus on RO_2 isomerization effects and corresponding changes in α-pinene product distributions.

Finally, we turn to indoor atmospheres, examining the impact of commercial air cleaners on indoor photochemistry and air quality under 222 nm germicidal lamps (GUV_{222}). GUV_{222} is effective at killing airborne pathogens, but it generates ozone in the indoor environment, thus initiating unwanted chemistry including SOA formation. Through environmental chamber experiments and modeling, we quantify the reduction of ozone and secondary pollutants by running commercial air cleaners concurrently with GUV_{222}.

These results highlight the potential benefits of air cleaners to improve indoor air quality across GUV_{222} and non-GUV_{222} settings.

Overall, this thesis connects several relevant areas of atmospheric photochemistry, helping improve our understanding of RO_2 chemistry and SOA formation from oxidation of biogenic VOCs, as well as characterizing indoor air quality implications of GUV_{222} and commercial air cleaning technologies.

Thesis supervisor: Jesse H. Kroll
Title: Peter de Florez Professor in Civil and Environmental Engineering, Chemical Engineering