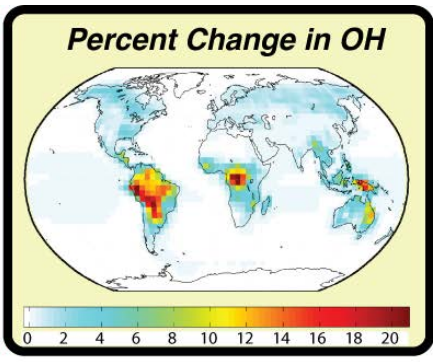
A product based perspective of secondary pollutant production: From the lab to the global scale



Tropospheric oxidation of volatile organic compounds (VOCs) is directly coupled to formation of secondary pollutants, in particular ozone and secondary organic aerosol, which affect climate and human health. Accurate mechanistic understanding of VOC oxidation across all spatial, temporal and chemical scales is critical to understanding how changing boundary conditions affect secondary pollutant concentrations. The potential to form secondary pollutants depends on (i) the amount of emitted VOCs, (ii) the rate of VOC oxidation determined oxidative capacity and by VOC concentrations, and (iii) the VOC oxidation product distribution.

In our work we combine novel measurements with product-based approaches that test whether observed reaction products are consistent with current mechanistic understanding of precursors and their reactivity. First, we present studies using new types of measurements of formaldehyde, a ubiquitous VOC oxidation product, that demonstrate secondary pollutant formation missing from models. Second, we utilize measurements of glyoxal, the smallest dicarbonyl, as a highly specific tracer of oxidative capacity and show that in a rural environment the overall VOC oxidation rate scales linearly with VOC concentration. Third, we combine the first synthesis of isoprene derived hydroperoxides, the dominant VOC oxidation products away from anthropogenic influence, with mechanistic chamber studies. These results show that previously existing limitations in availability of this important class of compounds may have biased our view of the role of hydroperoxides compared to products formed under anthropogenic influence. The large difference in the properties of the two types of oxidation products has a profound impact on oxidative capacity, VOC reactivity and the ability to form secondary organic aerosol.