

Oxidation flow reactors (OFRs): overview of recent field and modeling studies

Jose-Luis Jimenez (1), Brett B. Palm (1), Zhe Peng (1), Weiwei Hu (1), Amber M. Ortega (1), Rui Li (1), Pedro Campuzano-Jost (1), Douglas A. Day (1), Harald Stark (1), William H. Brune (2), Joost de Gouw (3), and Jason Schroder (1)

(1) University of Colorado at Boulder, Department of Chemistry & Biochemistry and CIRES, Boulder, Colorado, United States (jose.jimenez@colorado.edu), (2) Dept. of Meteorology, Penn State University, USA, (3) Chemical Sciences Division, NOAA, Boulder, USA

Oxidation flow reactors (OFRs) are popular tools for studying SOA formation and aging in both laboratory and field experiments. In an OFR, the concentration of an oxidant (OH, O₃, or NO₃) can be increased, leading to hours-months of equivalent atmospheric oxidation during the several-minute OFR residence time. Using gas- and particle-phase measurements from several recent field campaigns, we demonstrate SOA formation after oxidation of ambient air in an OFR. Typically, more SOA formation is observed from nighttime air than daytime air. This indicates that the concentration of SOA-forming gases in ambient air is relatively higher at night. Measured ambient VOCs are not able to explain the magnitude of SOA formation in the OFR, suggesting that typically unmeasured S/IVOCs (possibly VOC oxidation products or direct emissions) play a substantial intermediary role in ambient SOA formation. We also present highlights from recent OFR oxidant chemistry modeling studies. HO_x , Ox, and photolysis chemistry was modeled for two common OH production methods (utilizing 185+254 nm UV light, or 254 nm only). OH exposure (OHexp) can be estimated within a factor of ~ 2 using model-derived equations, and can be verified in situ using VOC decay measurements. OHexp is strongly dependent on external OH reactivity, which may cause significant OH suppression in some circumstances (e.g., lab/source studies with high precursor concentrations). UV light photolysis and reaction with oxygen atoms are typically not major reaction pathways. Modeling the fate of condensable low-volatility organic gases (LVOCs) formed in an OFR suggests that LVOC fate is dependent on particle condensational sink. E.g., for the range of particle condensational sink at a remote pine forest, anywhere from 20-80% of produced LVOCs were predicted to condense onto aerosols for an OHexp of ~ 1 day, with the remainder lost to OFR or sampling line walls. Similar to large chamber wall loss corrections, a correction is needed to relate OFR sampling to the atmosphere, where condensation onto aerosols is the dominant LVOC fate. At high OHexp (>20 days) in an OFR, LVOCs are predicted to be oxidized many times before they can condense onto particles, leading to formation of volatile fragmentation products that can no longer condense to form SOA. Changes to preexisting OA at high OHexp should be predominantly a result of heterogeneous oxidation. SOA yields specific to OFR oxidation were investigated using standard addition of individual VOCs into ambient air in an OFR. SOA yields in the OFR were consistent with laboratory large chamber yields.