Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.22660

Observationally constrained modeling of peroxy radical during an ozone episode in the Pearl River Delta region, China

YANLI ZHANG AND XINMING WANG

Guangzhou Institute of Geochemistry, Chinese Academy of Sciences

Presenting Author: zhang_yl86@gig.ac.cn

Peroxy radicals (RO2* = HO2 + RO2) play key roles in forming secondary air pollutants such as ozone, yet model underprediction of RO2* is a challenging radical closure problem. In this study, RO2* were measured by a dual-channel peroxy radical chemical amplification system during an ozone episode in October 2018 at an urban site in the Pearl River Delta region, China. The box model based on the Master Chemical Mechanism severely underpredicted RO2* levels, particularly at night and under high nitric oxide (NO) conditions. The observed-to-modeled ratio of RO2* increased from ~3 under 1 ppbv NO to ~46 under >10 ppbv NO with a missing RO2* source up to 5.8 ppbv hr−1. Observation data were used to constrain model predictions, and the results reveal that constraining nitrous acid (HONO) or glyoxal/methylglyoxal could not improve predictions, while constraining nitrate radicals (NO3) or other oxygenated volatile organic compounds (OVOCs), particularly phenolic compounds and improvements in their gas-phase mechanisms, could more effectively increase model-simulated RO2* concentrations. When OVOCs, NO3, and HONO were constrained, the simulated RO2* concentrations increased to the greatest extent with an observed-to-modeled RO2* ratio of 1.9 during the day and 1.3 at night, mainly due to the interaction between OVOCs and NO3 radicals. As the underestimated NO3 levels and the unmeasured reactive organic gases, as well as their unknown oxidation mechanisms, are among the major reasons for the underestimation of RO2*, upgraded atmospheric chemistry involving more OVOC species and more accurate NO3 would improve model-simulated RO2* concentrations, especially during nighttime.