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Glyoxal as a tracer of VOC oxidation chemistry: Comparison of measurements with model results for Blodgett Forest, California

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We present a study investigating Volatile Organic Compound (VOC) oxidation chemistry in the context of regional ozone (O_3) production during the BEARPEX 2007 and 2009 campaigns at Blodgett Forest Research Station (BFRS) in the Sierra Nevada mountains, CA. Measurements are compared with results from a regional model (US EPA CMAQ) and a zero dimensional (0-D) box model based on the Master Chemical Mechanism (MCM). We use glyoxal (CHOCHO) and formaldehyde (HCHO) as tracers for generalized oxidation processes and employ ratios of compounds (e.g. CHOCHO / HCHO, CHOCHO / MPAN) to study plume evolution as doing so attenuates the influence of meteorology. One of the goals of this study is to investigate the utility of glyoxal as a tracer of VOC oxidation chemistry for measurement/model comparisons, for which formaldehyde has served in the past. In this context, we investigate the discrepancies between models and measurements, and the degree to which these can be attributed to the representation of glyoxal chemistry (e.g. yields) or whether these discrepancies reflect VOC-HO_x-NO_x oxidation more generally, which has implications for ozone and secondary organic aerosol formation.

Model results from CMAQ and the 0-D box model substantially overestimate the absolute measured concentration of CHOCHO at BFRS, and the CMAQ model also shows poor agreement with the diurnal profile. The 0-D box model also overestimates CHOCHO in data taken at the Caltech Indoor Air Chambers, suggesting that 2^{nd}- and/or higher-generation yields of CHOCHO from isoprene are substantially overestimated in the MCM. 0-D model results that use attenuated 2^{nd}- and higher-generation production of CHOCHO from isoprene show enhanced agreement with chamber results.

We will present model results of the 0-D Box Model from BFRS employing these reduced yields that show improved agreement with measurements and also compare these results with the other models. We also present results obtained with two modifications of the CMAQ model; one with scaled glyoxal yields, and another in which overall VOC-HO_x-NO_x oxidation chemistry was adjusted in addition to the glyoxal yields. We will discuss the degree to which scaling glyoxal yields resolves the model-measurement disparities compared to factors such as HO_x and NO_x that affect general VOC oxidation chemistry. The latter factors affect CMAQ photochemistry more significantly, and might impact CMAQ O_3 predictions, which are currently excellent for BFRS.