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In situ glyoxal measurements in rural settings: loss processes, biogenic contribution and model - measurement comparison

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One crucial system to the chemical and radiative processes in the atmosphere is the oxidation of volatile organic compounds (VOCs). Oxidation processes of VOCs by nitrogen and hydrogen oxides are central to both smog and secondary organic aerosol (SOA) formation, both of which are implicated in human health and climate change. Glyoxal, the smallest dialdehyde, is linked to the oxidation of both anthropogenic and biogenic VOCs and forms SOA (Fu et al. JGR 113, D15303, 2008). Glyoxal has very few primary sources and is a higher generation oxidation product of biogenic VOCs; measurements of glyoxal thus provide insights unavailable via analysis of traditional oxygenated VOCs, such as formaldehyde, methyl vinyl ketone or methacrolein. Although there is a growing dataset of glyoxal mixing ratios for urban sites, there have been few studies using direct and fast measurement of glyoxal in rural areas, which contribute the majority of global glyoxal (Fu et al.). We present the first such measurements for two rural areas and a detailed analysis of the chemistry controlling the local glyoxal concentrations.

We have recently developed a laser-induced phosphorescence (LIP) instrument for high sensitivity (precision 2 pptv/min), fast, highly specific in situ measurement of glyoxal. The instrument participated in the BEARPEX 2007 (Huisman et al. Anal. Chem. 80, 5884, 2008) and PROPHET 2008 field campaigns. BEARPEX occurred at a site with high MBO and terpene emissions which was influenced by upwind isoprene emissions as well as the urban plume from Sacramento. The PROPHET 2008 field campaign was dominated by isoprene chemistry with only sporadic influence from anthropogenic emissions. The glyoxal mixing ratios observed during BEAPREX 2007 were significantly higher (up to 250 pptv) than during PROPHET 2008 (up to 80 pptv). We will present an overview of differences and similarities between the two measurement campaigns with respect to the atmospheric chemistry controlling glyoxal concentrations.
We will also present a detailed analysis of the BEARPEX 2007 campaign using photochemical box modeling: The results of the model show that the majority of glyoxal observed during that campaign was of biogenic origin and had a short (less than a few hours) lifetime for typical daytime conditions. The observed glyoxal concentrations show a pronounced and highly variable diurnal cycle. An analysis of the individual production and loss processes controlling glyoxal concentrations will be presented along with analysis of the relationship between the observed glyoxal concentrations to biogenic and anthropogenic emissions during BEARPEX 2007.

Results of a study exploring the utility of nighttime observations of glyoxal, made possible by the high sensitivity of the Madison LIP instrument, as a tool for analyzing nighttime OH concentrations and uptake of glyoxal onto aerosol as a sink will be presented. This high sensitivity allowed fast measurements which also revealed a pronounced but brief (less than 15 minute) increase in glyoxal some mornings during BEARPEX 2007 which was not observed during the PROPHET 2008 campaign. This spike was typically observed on days that had a temporally coinciding and similarly brief decrease in ozone concentrations. We will present results of our box model to identify potential processes which explain this feature.