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Closing the peroxy acetyl nitrate budget: observations of acyl peroxy nitrates (PAN, PPN, and MPAN) during BEARPEX 2007

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Abstract. Acyl peroxy nitrates (APNs, also known as PANs) are formed from the oxidation of aldehydes and other oxygenated VOC (oVOC) in the presence of NO₂. There are both anthropogenic and biogenic oVOC precursors to APNs, but a detailed evaluation of this chemistry against observations has proven elusive. Here we describe measurements of PAN, PPN, and MPAN along with the majority of chemicals that participate in their production and loss, including OH, HO₂, numerous oVOC, and NO₂.

Observations were made during the Biosphere Effects on AeROsols and Photochemistry Experiment (BEARPEX 2007) in the outflow of the Sacramento urban plume. These observations are used to evaluate a detailed chemical model of APN ratios and concentrations. We find that the ratios of APNs are nearly independent of the loss mechanisms and thus an especially good test of our understanding of their sources. We show that oxidation of methylvinyl ketone, methacrolein, methyl glyoxal, biacetyl and acetaldehyde are all significant sources of the PAN+peroxy acetyl (PA) radical reservoir, accounting for 26%, 2%, 7%, 20%, and 45%, of the production rate on average during the campaign, respectively. At high temperatures, when upwind isoprene emissions are highest, oxidation of non-acetaldehyde PA radical sources contributes over 60% to the total PA production rate, with methylvinyl ketone being the most important of the isoprene-derived sources. An analysis of absolute APN concentrations reveals a missing APN sink that can be resolved by increasing the PA+ΣRO₂ rate constant by a factor of 3.

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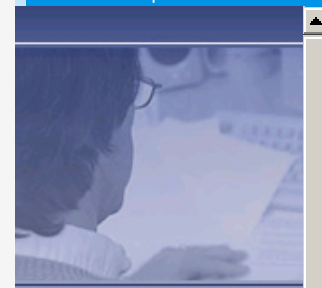
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