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Integrated multi-instrument assessment of gas and particle phase very reactive biogenic compounds in and above a forest canopy during the BEARPEX 2007 campaign

D. M. Matross (1), N. C. Bouvier-Brown (1), D. R. Worton (1), A. H. Goldstein (1)
(1) Department of Environmental Science, Policy, and Management, University of California, Berkeley (dmatross@nature.berkeley.edu; Ph. +1 510 643 6449; Fax +1 510 643 5098)

The environmental controls and chemical fate of very reactive biogenic emissions in the canopy and boundary layer above forests remain largely unexplained. We present a group of complimentary new measurements targeting very reactive biogenic compounds in the boundary layer taken from a 17-meter tower during the Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX) experiment during late summer 2007. A five-level gradient of proton transfer reaction mass spectrometer (PTR-MS) concentration measurements provide insight into the vertical structure of chemical and transport dynamics of a range of compounds within and just above a mixed pine canopy in California, while PTR-MS eddy covariance flux measurements give quantitative constraints on net exchange between the canopy and overlying atmosphere. We derive information on speciation and temporal dynamics from two particularly rich hourly in-situ gas chromatography (GC) datasets, one focused on gas phase measurements and the other employing thermal desorption aerosol GC mass spectrometry (TAG) to determine partitioning of ambient low volatility compounds between the gas and particle phases. A small set of marker compounds including methyl chavicol were detected by all three instruments in high enough concentrations to quantitatively relate the different methods. In conjunction with ancillary measurements taken by over fifteen collaborating research groups, we use an integrated approach to elucidate factors controlling biogenic emissions, gas-particle transitions,

and exchange with the overlying atmosphere. We demonstrate that because individual terpenoid species range across a broad envelope of reactivity and emission that new, more complex descriptive techniques will be required to quantify the bulk exchange of very reactive biogenic compounds to the atmosphere and their net effect on secondary particle formation.