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The bi-directional exchange of oxygenated VOCs between a loblolly pine (*Pinus taeda*) plantation and the atmosphere

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Abstract. Using new in-situ field observations of the most abundant oxygenated VOCs (methanol, acetaldehyde, acetone, C_3/C_4 carbonyls, MVK+MAC and acetic acid) we were able to constrain emission and deposition patterns above and within a loblolly pine *(Pinus taeda)* plantation with a sweetgum (*Liquidambar styraciflua*) understory. During the day canopy scale measurements showed significant emission of methanol and acetone, while methyl vinyl ketone and methacrolein, acetaldehyde and acetic acid were mainly deposited during the day. All oxygenated compounds exhibited strong losses during the night that could not be explained by conventional dry deposition parameterizations. Accompanying leaf level measurements indicated substantial methanol and acetone emissions from loblolly pine. The exchange of acetaldehyde was more complex. Laboratory measurements made on loblolly pine needles indicated that acetaldehyde may be either emitted or taken up depending on ambient concentrations, with the compensation point increasing exponentially with temperature, and that mature needles tended to emit more acetaldehyde than younger needles. Canopy scale measurements suggested mostly deposition. Short-term (approx. 2 h) ozone fumigation in the laboratory had no detectable impact on post-exposure emissions of methanol and acetone, but decreased the exchange rates of acetaldehyde. The emission of a variety of oxygenated compounds (e.g. carbonyls and alcohols) was triggered or significantly enhanced during laboratory ozone fumigation experiments. These results suggest that higher ambient ozone levels in the future might enhance the biogenic contribution of some oxygenated compounds. Those with sufficiently low vapor pressures may potentially influence secondary organic aerosol growth. Compounds recently hypothesized to be primarily produced in the canopy atmosphere via ozone plus terpenoid-type reactions can also originate from the oxidation reaction of ozone with leaf surfaces and inside the leaf. This needs to be taken into account when scaling up very reactive biogenic compounds.

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