The present study presents interesting results on some long-lasting controversies about reactive VOCs and previously reported (incl. this special issue) conflicting results on fast in-canopy photochemistry. In this context I would like to point out that we have previously shown that many OVOCs originally solely attributed to in-canopy gasphase oxidation at the Blodgett site, can also be a result of ozone induced surface or plant internal reactions (Karl et al., ACP, 2005). It also seems important to mention that the interpretation of in-canopy (gasphase) chemistry is often confounded by incomplete constraints on turbulent transport.

I find that many ‘chemistry-centric’ studies don’t give enough weight on the influence of canopy specific transport mechanisms. In the present study I wonder, whether the crude parameterization of in-canopy exchange can allow attributing model-measurement differences on the order of 20% solely to chemistry effects, in particular when no measurements of sigma(w)/u* are available to constrain the diffusion problem. In our previous work (Karl et al., JGR, 2004, ACP, 2005, JGR, 2007, BG, 2008 and ACP, 2009) we typically find that a good characterization of in-canopy turbulence profiles is crucial for a quantitative analysis of flux and concentration profiles. As an example Figure 1 shows two sigma(w)/u* parameterizations (based on Raupach, 1989) that were obtained from measured sigma(w)/u* profiles at two different pine ecosystems during recent years. The first profile was obtained at a loblolly pine forest in North Carolina (Karl et al., 2005), the second at a ponderosa pine forest in Colorado (Manitou SRM). Based on an exact implementation of Raupach’s formulation (including the parameterized near-field effect) these two turbulence profiles result in a generic flux, that is different by as much as 36% (i.e. solving for the inverse problem). Here I assume a tracer concentration profile that is typically observed for a net emission flux at the top of the canopy. The relative in-canopy flux divergence ratio can exhibit even more dramatic differences within the canopy (e.g. reversing the sign of the flux gradient: Figure 2). By tuning the turbulent parameterization to observed concentration profiles, modeled differences in emission, chemistry and deposition patterns of chemicals reported by Wolfe et al. (2010) could be partially or completely masked by physical rather than chemical effects alone. In light of these uncertainties I would argue that a 20% difference between modeled and observed ozone fluxes represents an astonishingly good agreement.

Figure 1: sigma(w)/u* profiles measured at two different pine forests, which are both comparable to the Blodgett ecosystem (z/h=1: top of the canopy)

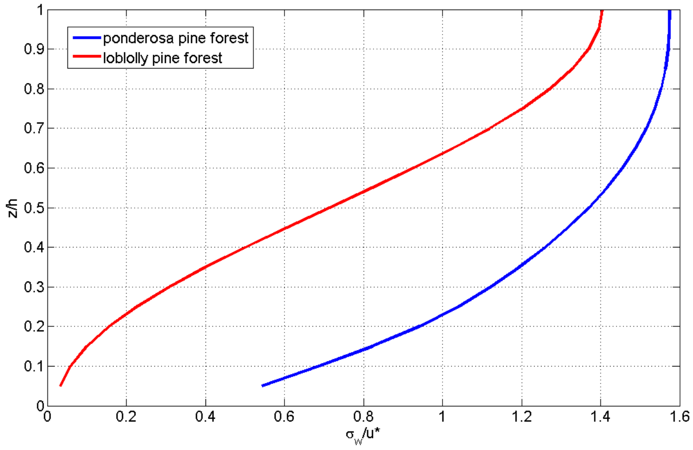

Figure 2: Relative difference of dF/dz profiles for the two turbulence parameterizations shown in Figure 1 (case 1: loblolly pine; case 2: ponderosa pine). The sensitivity run is done for an inert tracer, where a concentration profile is prescribed. The difference of the net emission flux (at the top of the canopy) in this case is about 36%.