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Constraining the concentration of the hydroxyl radical in a stratocumulus-topped marine boundary layer from sea-to-air eddy covariance flux measurements of dimethylsulfide

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Abstract. The hydroxyl radical (OH) is an important oxidant in the troposphere due to its high reactivity and relative abundance. Measuring the concentration of OH in situ, however, is technically challenging. Here we present a simple method of estimating an OH-equivalent oxidant concentration ("effective OH") in the marine boundary layer (MBL) from the mass balance of dimethylsulfide (DMS). We use shipboard eddy covariance measurements of the sea-to-air DMS flux from the Vamos Ocean-Cloud-Atmosphere-Land Study Regional Experiment (VOCALS-REx) in October and November of 2008. The persistent stratocumulus cloud-cover off the west coast of South America and the associated strong inversion between MBL and the free troposphere (FT) greatly simplify the dynamics in this region and make our budget estimate possible. From the observed diurnal cycle in DMS concentration, the nighttime entrainment velocity at the inversion is estimated to be 4 mm s^{-1}. We calculate $1.4(\pm0.2)\times10^6$ OH molecules cm^{-3} from the DMS budget, which represents a monthly effective concentration and is well within the range of previous estimates. Furthermore, when linearly proportioned according to the intensity of solar flux, the resultant diel OH profile, together with DMS surface and entrainment fluxes, enables us to accurately replicate the observed diurnal cycle in DMS (correlation coefficient over 0.9). The nitrate radical (NO_3) is found to have little contribution to DMS oxidation during VOCALS-REx. An upper limit estimate of 1 pptv of bromine oxide radical (BrO) would account for 30% of DMS oxidation and lower the OH concentration to $1.0)\times10^6$ OH molecules cm^{-3}. Our effective OH estimate includes the oxidation of DMS by such radicals.

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