

3.139 The atmospheric reactivity of the NO₃ radical.

Early Career Scientist

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Abstract:

We describe the first direct measurements of the total reactivity of NO_3 in ambient air, in which cavity-ring-down spectroscopy is used to monitor the loss synthetically generated NO_3 after reacting with ambient trace-gases in a flow-tube. The instrument can measure NO_3 loss rate constants between 0.005 s^{-1} and 45 s^{-1} with an uncertainty of 16 % in the center of its dynamic range.

Results from the deployment of this instrument in a boreal forest in southern Finland and a rural mountain site in southern Germany are presented. In both cases, NO_3 reactivity was driven by local meteorology coupled with biogenic emissions and displayed a strong vertical gradient with the highest reactivity measured below canopy level in the boreal forest. Very low NO_3 reactivities were observed in the residual layer. Comparison of the measured NO_3 reactivity with measurements of Volatile Organic Compounds (VOCs) indicated that the reactivity is dominated by reaction with monoterpenes, though a significant fraction of reactivity remained unattributed. During daytime, at both sites, more than 25% of the NO_3 formed was removed via reaction with biogenic volatile organic compounds (BVOCs), implying a significant daytime loss of NO_x and formation of organic nitrates and secondary organic aerosol via NO_3 chemistry even though the nitrate radical is generally considered to be of importance at night.