

# Nighttime nitrate radical chemistry at Appledore Island, Maine during the 2004 International Consortium for Atmospheric Research on Transport and Transformation

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## Abstract

Trace gases including nitrogen dioxide ( $\text{NO}_2$ ), nitrate radical ( $\text{NO}_3$ ), ozone ( $\text{O}_3$ ), and a suite of volatile organic compounds (VOCs) were measured within the New England coastal marine boundary layer on Appledore Island (AI), Maine, USA as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field campaign. These measurements, together with local meteorological records and published kinetic data were used to investigate nighttime  $\text{NO}_3$  chemistry at AI during the period of 8–28 July 2004. Among the VOCs, isoprene, monoterpenes and dimethylsulfide (DMS) were the dominant  $\text{NO}_3$  reactants; on average, DMS accounted for  $51 \pm 34\%$  of the total reactivity. For three case studies,  $\text{NO}_3$  mixing ratios were calculated from measured parameters with resultant uncertainties of  $\leq 30\%$ . Discrepancies with measured  $\text{NO}_3$  appeared to result primarily from input parameter variability and exclusion of heterogeneous dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) chemistry. We indirectly determined that nighttime  $\text{NO}_3$  and  $\text{NO}_x$  ( $=\text{NO} + \text{NO}_2$ ) removal via  $\text{N}_2\text{O}_5$  chemistry (gas-phase + heterogeneous) was on average 51–54% and 63–66% of the total respectively. Our analysis suggested that the minimum average  $\text{NO}_3$  and  $\text{NO}_x$  removal via heterogeneous  $\text{N}_2\text{O}_5$  chemistry was  $\approx 10\%$  of the total. Reducing gas-phase  $\text{N}_2\text{O}_5$  reactivity in accord with Brown et al. (2006a) increased the importance of heterogeneous  $\text{N}_2\text{O}_5$  chemistry substantially. It is plausible that the latter pathway was often comparable to gas-phase removal of  $\text{NO}_3$  and  $\text{NO}_x$ . Overall, 24 h-averaged  $\text{NO}_x$  removal was  $\approx 11$  ppbv, with nighttime chemical pathways contributing  $\approx 50\%$ .