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Temporal variability, sources, and sinks of C_1-C_5 alkyl nitrates in coastal New England

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Abstract. Seven C_1-C_5 alkyl nitrates were measured both on the mainland and off the coast of New Hampshire using gas chromatographic techniques. Five separate data sets are presented to characterize the seasonal and diurnal trends and the major sources and loss processes of these compounds. Based on in situ measurements conducted at the University of New Hampshire (UNH) Atmospheric Observing Station at Thompson Farm (TF) located in southeast NH during winter (January–February) 2002, summer (June–August) 2002, summer (July–August) 2004, and on daily canister samples collected at midday from January 2004–February 2008, the median total alkyl nitrate mixing ratio ($\Sigma RONO_2$) was 23–25 pptv in winter and 14–16 pptv in summer. During summers 2002 and 2004, $MeONO_2$ decreased overnight and reached minimum hourly average mixing ratios in the early morning. Comparison with wind speed and trace gas trends suggested that dry deposition contributed to the early morning $MeONO_2$ minimum which is a previously unaccounted for removal mechanism. The mean dry deposition rate and velocity of $MeONO_2$ was estimated to be -0.5 nmol m^{-2} hr^{-1} and 0.13 cm s^{-1}, respectively. Results from ambient air and surface seawater measurements made onboard the NOAA R/V Ronald H. Brown in the Gulf of Maine during the 2002 New England Air Quality Study and from ambient canister samples collected throughout the Great Bay estuary in August 2003 are also presented. Comparisons between the alkyl nitrate trends with anthropogenic and marine tracers suggest that a marine source of alkyl nitrates is not significant in coastal New England. Given the apparent prominence of a secondary source, comparisons between observed and predicted alkyl nitrate/parent hydrocarbon ratios were made which demonstrated that background mixing ratios have a continuous and prevalent influence on the alkyl nitrate distribution.

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