Deviations from ozone photostationary state during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign: Use of measurements and photochemical modeling to assess potential causes

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Abstract

Nitric oxide (NO) and nitrogen dioxide (NO_2) were monitored at the University of New Hampshire Atmospheric Observing Station at Thompson Farm (TF) during the ICARTT campaign of summer 2004. Simultaneous measurement of ozone (O_3), temperature, and the photolysis rate of NO_2 (j_{NO2}) allow for assessment of the O_3 photostationary state (Leighton ratio, Φ). Leighton ratios that are significantly greater than unity indicate that peroxy radicals (PO_2), halogen monoxides, nitrate radicals, or some unidentified species convert NO to NO_2 in excess of the reaction between NO and O_3. Deviations from photostationary state occurred regularly at TF ($1.0 \leq \Phi \leq 5.9$), particularly during times of low NO_x ($NO_x = NO + NO_2$). Such deviations were not controlled by dynamics, as indicated by regressions between Φ and several meteorological parameters. Correlation with j_{NO2} was moderate, indicating that sunlight probably controls nonlinear processes that affect Φ values. Formation of PO_2 likely is dominated by oxidation of biogenic hydrocarbons, particularly isoprene, the emission of which is driven by photosynthetically active radiation. Halogen atoms are believed to form via photolysis of halogenated methane compounds. Nitrate radicals are believed to be insignificant. Higher Φ values are associated with lower mixing ratios of isoprene and chloroiodomethane and lower ratios of NO_x to total active nitrogen, indicating that photochemical aging may very well lead to increased Φ values. PO_2 levels calculated using a zero-dimensional model constrained by measurements from TF can account for 71% of the observed deviations on average. The remainder is assumed to be associated with halogen atoms, most likely iodine, with necessary mixing ratios up to 0.6 or 1.2 pptv, for chlorine and iodine, respectively.

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