



Observations of Nighttime HONO in an Urban Area: Steady States, Dynamic Equilibrium States and Reversible Reservoirs

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Nitrous acid (HONO) is an important radical precursor in the troposphere. Recent consensus suggests that HONO is formed in the dark through the heterogeneous hydrolysis of NO_2 on surfaces ($2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3$), largely dominated by hydrolysis on ground surfaces and a smaller contribution from aerosol surfaces. Frequently a steady state of HONO is observed ($d\text{HONO}/dt \sim 0$) at night, which has been ascribed to a balance between heterogeneous formation and dry deposition. The fate of the surface deposited HONO remains an open question with the possibilities including the permanent loss of N(III), accumulation of surface reservoirs of N(III) at night, and/or a full dynamic equilibrium that partitions HONO between the atmosphere and water on the surface. Surface reservoirs of N(III) accumulated at night could act as a source of HONO the next day. Here we report measurements of HONO by DOAS in Toronto for a 1-year period. Of interest is the frequently observed phenomena of a fast approach to a steady state at sunset with rates of increase of $d[\text{HONO}]/dt = 1.4 \text{ ppb/hr}$ (with snow cover) and long periods in which the mixing ratio of HONO is constant with a median level of $\sim 1.1 \text{ ppb}$. We discuss these observations in the context of the steady state being attributable to a dynamic equilibrium state.