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The relationship between nighttime formation of gaseous HONO and nocturnal stability in an urban environment

Robert McLaren (1), Patryk Wojtal (1), and Peter Taylor (2)

(1) York University, Centre for Atmospheric Chemistry, Toronto, Canada (rmclaren@yorku.ca, 416-736-5411), (2) York University, Earth and Space Science & Engineering, Toronto, Canada

Nitrous acid (HONO) is an important radical precursor in the troposphere that accumulates overnight giving rise to a significant photolytic production of the hydroxyl radical, OH, in the boundary layer during early morning hours the next day. It is understood that HONO is formed in the dark through the heterogeneous hydrolysis of NO_2 on surfaces (2 NO_2+ H_2O -> HONO + HNO_3) in a first order process, largely dominated by hydrolysis on ground surfaces and a smaller contribution from aerosol surfaces. Despite progress, the dark heterogeneous mechanism of HONO formation is still not well understood, mirroring our lack of consensus on the daytime production of HONO. We have measured HONO at night in an urban area (York University, Toronto, Canada) by DOAS for over one year. This rich dataset was analyzed with a view to understanding the nocturnal formation mechanism, and possible links to the daytime HONO formation mechanism. Frequently, "steady-states" of HONO are observed at night; d[HONO]/dt $\sim$ 0, which follow after a rapid buildup of HONO during sunset at rates of several ppb hr^{-1}. These steady-state levels of HONO are found to be independent of the mixing ratio of NO_2 throughout the night. On other occasions, steady-states are not observed and HONO continues to increase throughout the night, highly correlated with the levels of NO_2 d([HONO]/[NO_2])/dt $\sim$ 0). We have found that a very significant predictor of the type of behavior is the nocturnal stability of the atmosphere, measured by the thermal gradient, $\Delta T = T_{9.5m} - T_{1.0m}$, and wind speed. The steady-state behavior is found to occur almost exclusively on unstable nights with higher wind speeds and $\Delta T \sim 0$, when mixing of air in the lower atmosphere is more efficient. The non steady-state behavior of HONO is observed on stable nights with low wind speeds and large thermal gradients, $\Delta T > 2^oC$ indicating limited vertical mixing. The observation of NO_2 independent steady-states of HONO under conditions of efficient nocturnal mixing suggest that the steady-state may result from an equilibrium between a surface reservoir source of HONO, reminiscent of those observed in the polluted marine boundary layer at night (Wojtal et al., Atmos. Chem. Phys., 11, 3243-3261, 2011).