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Traffic Emissions of Radical Precursors and Related Species as Observed and Modeled at an Urban Highway Junction in Houston/Texas

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Nitrous acid (HONO) and formaldehyde (HCHO) are important precursors for radicals and are believed to favor ozone formation significantly. Traffic emissions data for both compounds is scarce. Here we report results from continuous ambient air measurements of HONO, HCHO, carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides ($NO/NO_2/NO_x$), and peroxyacyl nitrates (PANs) taken at an Highway Junction in Houston/Texas from July 15 - October 15, 2009. The observational data was compared to emission estimates from currently available mobile emissions models (MOBILE6; MOVES). Observations indicated a molar CO versus NO_x ratio of 6.01±0.15 (r2 = 0.91), which is in agreement with other field studies. Both, MOBILE6 and MOVES, overestimate this emission ratio by 92% and 24%, respectively. For HCHO/CO an overall slope of 3.14±0.14 g HCHO / kg CO was observed. While MOBILE6 largely underestimates this ratio by 77%, MOVES calculates somewhat higher HCHO/CO ratios (1.87) than MOBILE6, but is still significantly lower than the observed ratio. MOVES shows high HCHO/CO ratios during the early morning hours due to heavy duty diesel off-network emissions. The differences of the modeled CO/NO_x and HCHO/CO ratios are largely due to higher NO_x and HCHO emissions in MOVES (30% and 57%, respectively, increased from MOBILE6 for 2009), as CO emissions were about the same in both models. The observed $HONO/NO_x$ emission ratio is around 0.017±0.0009 kg HONO / kg NO_x which is twice as high as in MOVES. The observed NO_2/NO_x emission ratio is around 0.16±0.01 kg NO_2 / kg NO_x, which is a bit more than 50% higher than in MOVES. MOVES overestimates the CO/CO_2 emission ratio by a factor of 3 compared with the observations, which is 0.0033±0.0002 kg CO / kg CO_2. This as well as CO/NO_x overestimation is coming from light duty gasoline vehicles.