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Analysis of Strong Wintertime Ozone Events in an Area of Extensive Oil and Gas Extraction

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During recent years, elevated ozone (O_3) values have been observed repeatedly in the Upper Green River Basin (UGRB), Wyoming during wintertime. This paper presents an analysis of high ozone days in late winter 2011 (1-hour average up to 166 ppbv). Intensive Observational Periods (IOPs) were performed which included comprehensive surface and boundary layer measurements. Low windspeeds in combination with low mixing layer heights ($\sim$50 m agl) are essential for accumulation of pollutants. Air masses contain substantial amounts of reactive nitrogen (NO_x) and non-methane hydrocarbons (NMHC) emitted from fossil fuel exploration activities in the Pinedale Anticline. On IOP days in the morning hours reactive nitrogen (up to 69%), then aromatics and alkanes (each $\sim$10-15%; mostly ethane and propane) are major contributors to the hydroxyl (OH) reactivity. This time frame largely coincides with lowest NMHC/NO_x ratios ($\sim$50), reflecting a relatively low NMHC mixture, and a change from a NO_x-limited regime towards a NMHC limited regime.
OH production on IOP days is mainly due to nitrous acid (HONO). On a 24-hr basis and as determined for a measurement height of 1.80 m above the surface HONO photolysis on IOP days can contribute $\sim$83% to OH production on average, followed by alkene ozonolysis ($\sim$9%). Photolysis by ozone and HCHO photolysis contributes about 4% each to hydroxyl formation. High HONO levels (maximum hourly median on IOP days: 1,096 pptv) are favored by a combination of shallow boundary layer conditions and enhanced photolysis rates due to the high albedo of the snow surface. HONO is most likely formed through (i) abundant nitric acid (HNO_3) produced in atmospheric oxidation of NO_x, deposited onto the snow surface and undergoing photo-enhanced heterogeneous conversion to HONO and (ii) combustion related emission of HONO. HONO production is confined to the lowermost 10 m of the boundary layer. HONO, serves as the most important precursor for OH, strongly enhanced due to the high albedo of the snow cover.