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Observations of the diurnal and seasonal trends in nitrogen oxides in the western Sierra Nevada

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Abstract. Observations of speciated nitrogen oxides, namely NO_2, total peroxy nitrates (ΣPNs), total alkyl nitrates (ΣANs), and HNO_3 by thermal dissociation laser induced fluorescence (TD-LIF), and supporting chemical and meteorological measurements at Big Hill (1860 m), a high elevation site in California's Sierra Nevada Mountains, are described. From May through October, terrain-driven winds in the region routinely bring air from Sacramento, 100 km southwest of the site, upslope over oak and pine forests to Big Hill during the day, while at night, the site often samples clean, dry air characteristic of the free troposphere. Winter differs mainly in that the meteorology does not favour the buildup of Sacramento's pollution over the Sierra Nevada range, and the urban-influenced air that is seen has been less affected by biogenic VOC emissions, resulting in longer lifetime for NO_2 and a predominance of the inorganic forms of nitrogen oxides.

Summertime observations at Big Hill can be compared with those from Granite Bay, a Sacramento suburb, and from the University of California's Blodgett Forest Research Station to examine the evolution of nitrogen oxides and ozone within the urban plume. Nitrogen oxide radicals (NO and NO_2), which dominate total nitrogen oxides (NO_y) at Granite Bay, are rapidly converted into HNO_3, ΣPNs, and ΣANs, such that these compounds contribute 29, 30, and 21% respectively to the NO_y budget in the plume at Big Hill. Nevertheless, the decreasing concentrations of NO_2 as the plume is advected to Big Hill lead to decreases in the production rate of HNO_3 and ozone. The data also demonstrate the role that temperature plays in sequestering NO_2 into peroxy nitrates, effectively decreasing the rate of ozone production. The important contribution of ΣANs to NO_y in the region suggests that they should be considered with regards to export of NO_y from the boundary layer. Nocturnal observations of airmasses characteristic of the free troposphere showed lower NO_y concentrations, which were dominated by HNO_3 with a relatively small contribution from the organic nitrates.

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