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Long term measurements of NO$_{3}$ radical at a semi-arid urban site: Extreme concentration events and their oxidation capacity

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Nitrate radical (NO_3), an important nighttime tropospheric oxidant, was measured continuously for two years (July 2005-September 2007) in Jerusalem, a semi-arid urban site, by long-path differential optical absorption spectroscopy (LP-DOAS). Joint measurements with the University of Heidelberg's LP-DOAS showed good agreement (r=0.94). Extreme episodes of NO_3 were measured during this period, with maximum mixing ratios above 800 ppt, two-fold greater than measured anywhere else. The unique chemistry of these extreme levels is a consequence of several factors: (i) an increase in ozone concentrations parallel to a substantial decrease in relative humidity during the night, (ii) mean nighttime NO_2 levels above 10 ppbv preventing a deficiency in NO_3 precursors, (iii) negligible NO levels during the night, and (iv) a substantial decrease in the loss processes leading to lower degradation frequencies and allowing the NO_3 lifetimes to build up to a maximum mean of 25 minutes. The results indicate that for these extreme events, the major sink pathway for NO_3 was direct homogeneous gas phase reactions with VOCs. We have found that compared to OH and O_3, NO_3 extreme events are responsible for approximately 70% of the oxidation of total VOCs and nearly 75% of the olefinic VOCs, twice the oxidation potential of the OH radical for the VOC's. These results establish the NO_3 radical as a significant atmospheric oxidant in Jerusalem and as a predominant contributor to VOC degradation in urban atmospheres.