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The oxidation capacity of the city air of Santiago, Chile

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The oxidation capacity of the highly polluted urban area of Santiago, Chile has been studied during an extensive summer measurement campaign carried out from the 8^{th}-20^{th} March, 2005. One focus was the hydroxyl (OH) radical budget, for which a simple quasi-stationary-state model has been constrained with simultaneous measurements of HONO (using a highly sensitive LOPAP instrument), HCHO, O_3, CO, NO, NO_2, J(O^1D), J(NO_2), 20 alkenes and meteorological parameters. A one dimensional photochemical box model based on the Master Chemical Mechanism (MCMv3.1, http://mcm.leeds.ac.uk/MCM/) has been used to estimate the production rates and total radical budgets (including OH, HO_2 and RO_2) throughout the day. Mixing ratios of the main OH radical precursors, HONO, HCHO and O_3, were found to be in the range 0.8-7 ppbV (HONO), 0.9-11 ppbV (HCHO) and 0-125 ppbV (O_3). Both models showed the same OH radical budget during the day time, which indicates that the primary OH sources included in the simple QSS model are predominant. HONO photolysis was shown to be the most important primary OH radical source, comprising alone more than 50 % of the total production rate, followed by alkene ozonolysis ($\sim$ 22 %) and photolysis of HCHO ($\sim$ 17 %) and O_3 ($\sim$ 9 %). The high calculated maximum and average daytime (08:00 -19:00 h) OH production rates from HONO photolysis of 3.1 ppbV h^{-1} and 1.7 ppbV h^{-1}, respectively, demonstrate the unique geographical situation of Santiago. Based on the experimental results a strong photochemical daytime source of HONO is proposed.